UNIVERSITY OF MAINE
LIBRARY

Class no. ~~540.6~~
Book no. ~~L486~~
Accession no. 80,090

v.22

LIBRARY
OF THE

LIBRARY
UNIV OF MAINE

ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY.

LIBRARY
UNIV OF MAINE

ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY

FOR 1925.

ISSUED BY THE CHEMICAL SOCIETY.

Committee of Publication:

Chairman: N. V. SIDGWICK, M.A., Sc.D., F.R.S.

H. B. BAKER, C.B.E., D.Sc., F.R.S.
E. C. C. BALY, C.B.E., F.R.S.
H. BASSETT, D.Sc., Ph.D.
O. L. BRADY, D.Sc.
A. W. CROSSLEY, C.M.G., C.B.E., F.R.S.
F. G. DONNAN, C.B.E., M.A., F.R.S.
H. W. DUDLEY, O.B.E., M.Sc., Ph.D.
U. R. EVANS, M.A.
J. J. FOX, O.B.E., D.Sc.
C. S. GIBSON, O.B.E., M.A.
A. J. GREENAWAY, F.I.C.
I. M. HEILBRON, D.S.O., D.Sc.
T. A. HENRY, D.Sc.
C. K. INGOLD, D.Sc., F.R.S.
H. MCCOMBIE, D.S.O., M.C., D.Sc.
J. I. O. MASSON, M.B.E., D.Sc.
W. H. MILLS, Sc.D., F.R.S.
T. S. MOORE, M.A., B.Sc.
G. T. MORGAN, O.B.E., D.Sc., F.R.S.
J. R. PARTINGTON, M.B.E., D.Sc.
J. C. PHILIP, O.B.E., D.Sc., F.R.S.
R. H. PICKARD, D.Sc., F.R.S.
T. S. PRICE, C.B.E., D.Sc., F.R.S.
F. L. PYMAN, D.Sc., F.R.S.
J. F. THORPE, C.B.E., D.Sc., F.R.S.
W. P. WYNNE, D.Sc., F.R.S.

Editor:

CLARENCE SMITH, D.Sc.

Indexer:

MARGARET LE PLA, B.Sc.

Contributors:

A. J. ALLMAND, M.C., D.Sc.
W. T. ASTBURY.
Sir W. H. BRAGG, K.B.E., F.R.S.
H. V. A. BRISCOE, D.Sc.
W. CLAYTON, D.Sc.
J. E. COATES, O.B.E., D.Sc.
C. DORÉE, M.A., D.Sc.
J. C. DRUMMOND, D.Sc.
B. A. ELLIS, M.A.
J. J. FOX, O.B.E., D.Sc.
T. A. HENRY, D.Sc.
C. K. INGOLD, D.Sc., F.R.S.
H. J. PAGE, M.B.E., B.Sc.
L. J. SPENCER, M.A., Sc.D., F.R.S.

Vol. XXII.

LONDON:

GURNEY & JACKSON, 33 PATERNOSTER ROW, E.C.4.

1926.

PRINTED IN GREAT BRITAIN BY
RICHARD CLAY & SONS, LIMITED,
BUNGAY, SUFFOLK.

YMAGIL
UNIV OF MAINE

CONTENTS.

PAGE

GENERAL AND PHYSICAL CHEMISTRY. By J. E. Coates, O.B.E., D.Sc. 11

INORGANIC CHEMISTRY. By H. V. A. Briscoe, D.Sc. . . . 42

ORGANIC CHEMISTRY :—

Part I.—Aliphatic Division. By Charles Dorée, M.A., D.Sc. . . 67

Part II.—Homocyclic Division. By C. K. Ingold, D.Sc., F.R.S. . 105

Part III.—Heterocyclic Division. By T. A. Henry, D.Sc. . . 132

ANALYTICAL CHEMISTRY. By J. J. Fox, O.B.E., D.Sc., and B. A. Ellis, M.A. 168

BIOCHEMISTRY. By J. C. Drummond, D.Sc., and H. J. Page, M.B.E., B.Sc. 194

CRYSTALLOGRAPHY. By W. T. Astbury and Sir W. H. Bragg, K.B.E., F.R.S. 240

MINERALOGICAL CHEMISTRY. By L. J. Spencer, M.A., Sc.D., F.R.S. 259

COLLOID CHEMISTRY. By William Clayton, D.Sc. . . . 281

PHOTOCHEMISTRY, 1914–1925. By A. J. Allmand, M.C., D.Sc. . . 333

80, 090

TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

Abbreviated Title.	Journal.
A.	Abstracts in Journal of the Chemical Society, or issued by the Bureau of Chemical Abstracts.*
Amer. Chem. J.	American Chemical Journal.
Amer. J. Anat.	American Journal of Anatomy.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Sci.	American Journal of Science.
Amer. Min.	American Mineralogist.
Anal. Asoc. Quím. Argentina	Anales de la Asociación Química Argentina.
Anal. Fís. Quím.	Anales de la Sociedad Espanõla Física y Química.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Appl. Biol.	Annals of Applied Biology.
Ann. Bot.	Annals of Botany.
Ann. Chim.	Annales de Chimie.
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industries à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim. Appl.	Annali di Chimica Applicata.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. Faculté Sci. Marseille	Annales de la Faculté des Sciences de Marseille.
Ann. Physik	Annalen der Physik.
Ann. Phys. Chem.	Annalen der Physik und Chemie.
Ann. Physique	Annales de Physique.
Ann. Report	Annual Reports of the Chemical Society.
Ann. Soc. Géol. Belge (*Bull.*)	Annales de la Société géologique de Belgique : (Bulletin).
Ann. Soc. Géol. Belge (*Publ. Congo Belge*)	Anales de la Société géologique de Belgique : (Publications relatives au Congo Belge).
Arch. di Patalog. e clin. Medica	Archivio di Patalogia e clinica Medica.
Arch. exp. Path. Pharm.	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Gynäk	Archiv für Gynäkologie.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Verdauungskr.	Archiv für Verdauungskrankheiten.
Arkiv Kem. Min. Geol.	Arkiv för Kemi, Mineralogi och Geologi.
Atti R. Accad. Lincei	Atti (Rendiconti, Memorie) della Reale Accademia Nazionale dei Lincei, classe di scienze fisiche, matematiche e naturali, Roma.
Australian J. Exp. Biol. Med. Sci.	Australian Journal of Experimental Biology and Medical Science.
Beitr. Chem. Physiol. Path.	Beiträge zür chemischen Physiologie und Pathologie.
Beitr. Kryst. Min.	Beiträge zür Krystallographie und Mineralogie.
Ber.	Berichte der Deutschen Chemischen Gesellschaft.
Ber. Deut. physikal. Ges.	Berichte der Deutschen physikalischen Gesellschaft.

* The year is not inserted in references to 1925.

Abbreviated Title.	Journal.
Biochem. J.	The Biochemical Journal.
Biochem. Z.	Biochemische Zeitschrift.
Boll. Chim. farm.	Bolletino Chimico farmaceutico.
Brennstoff Chem.	Brennstoff Chemie.
Brit. Assoc. Reports	British Association Reports for the Advancement of Science.
Bul. Soc. Chim. România	Bulétinul Societătei de Chimie din România.
Bull. Acad. Sci. Cracow	Bulletin international de l'Académie des Sciences de Cracovie.
Bull. Acad. Sci. Russie	Bulletin de l'Académie des Sciences de Russie.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. Chim. biol.	Bulletin de la Société de Chimie biologique.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Bull. U.S. Geol. Survey	Bulletin of the U.S. Geological Survey.
Cellulosechem.	Cellulosechemie.
Centr. Min.	Centralblatt für Mineralogie, Geologie und Paläontologie.
Chem. Listy	Chemické Listy pro Vědu a Průmysl. Organ de la "Ceská chemická Společnost pro Védu a Prûmysl."
Chem. News	Chemical News.
Chem. Umschau	Chemische Umschau auf dem Gebiete der Fette, Oele, Wachse, und Harze.
Chem. Weekblad	Chemisch Weekblad.
Chem. Ztg.	Chemiker Zeitung.
Chem. Zentr.	Chemisches Zentralblatt.
Chim. et Ind.	Chimie et Industrie.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
C. R. Acad. Sci. Russie	Comptes rendus de l'Académie des Sciences de Russie.
Compt. rend. Trav. Lab. Carlsberg	Comptes rendus des Travaux du Laboratoire Carlsberg.
Danske Vid. Selsk. Math.-fis. Medd.	Danske Videnskabernes Selskab, Mathematisk-fisiske Meddelelser.
Deutsch. Med. Wock.	Deutsche medizinische Wochenschrift.
Gazzetta	Gazzetta chimica italiana.
Geol. För. Förh.	Geologiska Föreningens i Stockholm Förhandlingar.
Giorn. Chim. Ind. Appl.	Giornale di Chimica Industriale ed Applicata.
Helv. Chim. Acta	Helvetica Chimica Acta.
Indian Forest Rec.	Indian Forest Records.
Ind. Eng. Chem.	Industrial and Engineering Chemistry.
Inst. Phys. Chem. Res. Tokyo	Institute of Physical and Chemical Research, Tokyo.
J.	Journal of the Chemical Society.
Jahrb. Min. Beil.-Bd.	Neues Jahrbuch für Mineralogie, Geologie und Paläontologie, Beilage-Band.
J. Agric. Res.	Journal of Agricultural Research.
J. Agric. Sci.	Journal of Agricultural Science.
J. Amer. Ceram. Soc.	Journal of the American Ceramic Society.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Amer. Med. Assoc.	Journal of the American Medical Association.
J. Amer. Pharm. Assoc.	Journal of the American Pharmaceutical Association.
J. Amer. Soc. Agron.	Journal of the American Society of Agronomy.
J. Assoc. Off. Agric. Chem.	Journal of the Association of Official Agricultural Chemists.
J. Biol. Chem.	Journal of Biological Chemistry.
J. Chem. Ind. Japan	Journal of Chemical Industry, Japan.
J. Chim. phys.	Journal de Chimie physique.
J. Exper. Med.	Journal of Experimental Medicine.
J. Fac. Eng. Tokyo	Journal of the Faculty of Engineering, Tokyo Imperial University.

Abbreviated Title.	Journal.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Gen. Physiol.	Journal of General Physiology.
J. Geol.	Journal of Geology.
J. Geol. Soc. Tokyo	Chishitsugaku Zasshi (Journal of the Geological Society of Tokyo).
J. Indian Chem. Soc.	Quarterly Journal of the Indian Chemical Society.
J. Indian Inst. Sci.	Journal of the Indian Institute of Science.
J. Indust. Hygiene	Journal of Industrial Hygiene.
J. Inst. Brewing	Journal of the Institute of Brewing.
J. Inst. Metals	Journal of the Institute of Metals.
J. Iron Steel Inst.	Journal of the Iron and Steel Institute.
J. Landw.	Journal für Landwirtschaft.
J. Oil Col. Chem. Assoc.	Journal of the Oil and Colour Chemists' Association.
J. Opt. Soc. Amer.	Journal of the Optical Society of America.
J. Path. Bact.	Journal of Pathology and Bacteriology.
J. Pharmacol.	Journal of Pharmacology and Experimental Therapeutics.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. Physique.	Journal de Physique.
J. Phys. Radium	Journal de Physique et le Radium.
J. pr. Chem.	Journal für praktische Chemie.
J. Roy. Soc. Western Australia	Journal of the Royal Society of Western Australia.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Scientific Instruments	Journal of Scientific Instruments.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Dyers Col.	Journal of the Society of Dyers and Colourists.
J. Soc. Leather Trades Chem.	Journal of the Society of Leather Trades' Chemists.
J. Soc. Phys. Chim. Russe. Univ. Leningrad	Journal de la Société Physico-Chimique Russe à l'Université de Leningrad.
J. S. Afr. Chem. Inst.	Journal of the South African Chemical Institute.
J. Text. Inst.	Journal of the Textile Institute.
J. Washington Acad. Sci.	Journal of the Washington Academy of Sciences.
Klin. Woch.	Klinische Wochenschrift.
Koll. Chem. Beihefte	Kolloidchemische Beihefte.
Kolloid Z.	Kolloid-Zeitschrift.
Landw. Jahrb.	Landwirtschaftliche Jahrbücher.
Landw. Versuchs-Stat.	Die Landwirtschaftlichen Versuchs-Stationen.
Mediz. Naturwiss Arch.	Medizinisch-naturwissenschaftliches Archiv.
Mem. Coll. Sci. Kyoto	Memoirs of the College of Science, Kyoto Imperial University.
Mem. Dept. Agric. India	Memoirs of the Department of Agriculture in India.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Mém. Soc. R. Sci. Liége	Mémoires de la Société R. des Sciences de Liége.
Mikrochem.	Mikrochemie.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Naturwiss	Die Naturwissenschaften.
P.	Proceedings of the Chemical Society.
Papierfabr.	Papier-Fabrikant.
Perf. Ess. Oil. Rec.	Perfumery and Essential Oil Record.
Pflüger's Archiv.	Archiv für die gesamte Physiologie des Menschen und der Thiere.
Pharm. J.	Pharmaceutical Journal.
Pharm. Weekblad	Pharmaceutisch Weekblad.

Abbreviated Title.	Journal.
Pharm. Ztg.	Pharmazeutische Zeitung.
Pharm. Zentr.	Pharmazeutische Zentralhalle.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Physical Rev.	Physical Review.
Physikal. Z.	Physikalische Zeitschrift.
Proc. Acad. Nat. Sci. Philadelphia	Proceedings of the Academy of Natural Sciences of Philadelphia.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. Colorado Sci. Soc.	Proceedings of the Colorado Scientific Society.
Proc. Indiana Acad. Sci.	Proceedings of the Indiana Academy of Science.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Nat. Acad. Sci.	Proceedings of the National Academy of Sciences.
Proc. Physical Soc.	Proceedings of the Physical Society of London.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Proc. Soc. Exp. Biol. Med.	Proceedings of the Society for Experimental Biology and Medicine.
Proc. U.S. Nat. Museum	Proceedings of the United States National Museum.
Quart. J. Exp. Physiol.	Quarterly Journal of Experimental Physiology.
Quart. J. Med.	Quarterly Journal of Medicine.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Rend. Accad. Sci. Fis. Mat. Napoli	Rendiconto dell'Academia delle Scienze Fisiche e Matematiche Napoli.
Rep. Imp. Ind. Res. Instit. Osaka, Japan	Reports of the Imperial Industrial Research Institute, Osaka, Japan.
Repert. Pharm.	Repertorium der Pharmazie.
Rev. gén. Coll.	Revue générale des Colloïdes.
Rev. gén. Sci.	Revue générale des Sciences pures et appliquées.
Rocz. Chem.	Roczniki Chemji organ Polskiego Towarzystwa Chemicznego.
Sci. Rep. Tôhoku Imp. Univ.	Science Reports, Tôhoku Imperial University.
Sitzungsber. Ges. Beförder. ges. Naturwiss. Marburg	Sitzungsberichte der Gesellschaft zür Beförderung der gesamten Naturwissenschaften zu Marburg.
Sitzungsber. Preuss. Akad. Wiss. Berlin	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
Skan. Arch. Physiol.	Skandinavisches Archiv für Physiologie.
Soil Sci.	Soil Science.
Stahl u. Eisen	Stahl und Eisen.
Svensk. Farm. Tids.	Svensk Farmaceutisk Tidskrift.
Tech. Rep. Tôhoku Imp. Univ.	Technology Reports of the Tôhoku Imperial University, Sendai, Japan.
Tids. Kemi Bergvaesen	Tidsskrift for Kemi og Bergvaesen.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Ceram. Soc.	Transactions of the Ceramic Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Univ. Toronto, Sch. Eng. Res. Bull.	University of Toronto School of Engineering Research, Bulletin.
Univ. Toronto Studies, Geol. Ser.	University of Toronto Studies, Geological Series.
U.S. Dept. Agric. Bull.	United States Department of Agriculture Bulletins.
Z. anal. Chem.	Zeitschrift für analytische Chemie.
Z. angew. Chem.	Zeitschrift für angewandte Chemie.
Z. anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie.
Z. Elektrochem.	Zeitschrift für Elektrochemie.
Z. Krist.	Zeitschrift für Krystallographie.

Abbreviated Title.	Journal.
Z. Metallk.	Zeitschrift für Metallkunde.
Z. Pflanz. Dung. . .	Zeitschrift für Pflanzenernährung und Düngung.
Z. Physik	Zeitschrift für Physik.
Z. physikal. Chem. . .	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Z. physiol. Chem. . .	Hoppe-Seyler's Zeitschrift für physiologsiche Chemie.
Z. tech. Physik . . .	Zeitschrift für technische Physik.
Z. Unters. Nahr.-Genussm .	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Z. Ver. Deut. Zucker Ind. .	Zeitschrift des Vereins der deutschen Zucker-Industrie.
Z. wiss. Photochem. . .	Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie.
Z. Zuckerind. Czechoslov. .	Zeitschrift für Zuckerindustrie der Cechoslovakischen Republik.

ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY.

GENERAL AND PHYSICAL CHEMISTRY.

The Velocity of Chemical Reactions.

The difficult fundamental problems of the kinetics of chemical reactions have continued to attract much discussion and experiment. The accepted view that reaction occurs through the agency of activated molecules which have acquired a critical increment of energy over the average tends to become more definite by the identification of activated states with higher quantum states of the molecule, and a solution of the problem may be expected to follow the further development of our knowledge of quantum mechanics as it affects the energy exchange between molecules.

R. C. Tolman [1] points out that the well-known expressions for uni- and bi-molecular reactions: $-dC/dt = kC = k'e^{-E/RT}C$, and $-dC/dt = kCC' = k'\sqrt{T} \cdot e^{-(E+E')/RT}CC'$, have previously been deduced only by assuming some possible but not inevitable mechanism, one fast enough to maintain the full Maxwell-Boltzmann quota of active molecules in the reacting system [2] or one involving radiation.[3] By a mathematical analysis based on the "principle of microscopic reversibility" [4] he derives these equations without assuming any specific mechanism, and concludes that they give the energy of activation under a wider variety of conditions than have hitherto been considered.

The main problem is to find a mechanism of energy transfer

[1] *J. Amer. Chem. Soc.*, 1925, **47**, 2652.

[2] R. Marcelin, *Ann. Physique*, 1915, [ix], **3**, 120; *A.*, 1915, ii, 328; J. Rice, *Brit. Assoc. Reports*, 1915, 397; W. H. Rodebush, *J. Amer. Chem. Soc.*, 1923, **45**, 606; *A.*, 1923, ii, 303; J. A. Christiansen and H. A. Kramers, *Z. physikal. Chem.*, 1923, **104**, 451; *A.*, 1924, ii, 28.

[3] J. Perrin, *Ann. Physique*, 1919, [ix], **11**, 5; *A.*, 1919, ii, 177; W. C. McC. Lewis, *J.*, 1918, **113**, 471; *Phil. Mag.*, 1920, [vi], **39**, 26; *A.*, 1920, ii, 100.

[4] "If we have a system in statistical equilibrium, the principle requires not only that the number of molecules in any given state shall remain constant, but that the number leaving that state in unit time by any particular path shall be made up by the entrance of an equal number of molecules by the reverse of that particular path" (R. C. Tolman, *loc. cit.*).

adequate to supply activated molecules at least as fast as they are used up by reaction. The position has been reviewed by M. Bodenstein,[5] R. C. Tolman,[6] and others.[7] In a purely thermal homogeneous gas reaction activation may be effected (*a*) by collisions, (*b*) by absorption of radiation. The simplest view is that activation results from the inelastic collision of two molecules of sufficiently high energy of translational motion relative to each other, the latter being converted into internal energy of activation. In a bimolecular change A + B = AB, reaction may depend on collision between [8] (*a*) A* + B, or (*b*) A* + B*, or (*c*) A + B, in the last case both being activated by the collision itself. Tolman [9] finds that the data for well-defined second-order reactions are compatible with (*b*) and (*c*), not with (*a*), but regards this as no proof of activation by collision. C. N. Hinshelwood [10] regards the experimental evidence as definitely in favour of (*c*), the heat of activation, E, being a real measure of the relative kinetic energy that the molecules must possess in order that reaction may occur on collision. On the other hand, activation by simple collision has been proved to be very far from adequate to maintain unimolecular reactions. The chance of two molecules of nitrogen pentoxide colliding with the high energy of 24700/N cal. is very small. The view recently put forward by Sir J. J. Thomson [11] that certain molecules accumulate by collision sufficient energy to cause dissociation implies an accelerating effect by an inert diluent, which is contrary to recent observation.[12]

The failure of simple collisions to account for the high rates of first-order reactions accompanied by such large energy of activation led J. A. Christiansen and H. A. Kramers [13] to propose the "hot molecule" theory whereby molecules are activated mainly by collisional transfer of the heat of reaction; thus for a unidirectional decomposition (regarded as exothermal): $AB \rightleftharpoons (AB)^* \longrightarrow [A^* + B^*] \longrightarrow A + B$. The complex of resultants *immediately after spontaneous decomposition* of (AB)* contains the heat of reaction as well

[5] *Z. Elektrochem.*, 1925, **31**, 343.
[6] *J. Amer. Chem. Soc.*, 1925, **47**, 1524; *A.*, ii, 799.
[7] *E.g.*, G. N. Lewis and D. F. Smith, *ibid.*, p. 1508; *A.*, ii, 799.
[8] A* signifies an activated molecule of A.
[9] *Loc. cit.*
[10] C. N. Hinshelwood and J. Hughes, *J.*, 1924, **125**, 1841; C. N. Hinshelwood and R. E. Burk, *Proc. Roy. Soc.*, 1924, *A*, **106**, 284; *A.*, 1924, ii, 751; C. N. Hinshelwood and C. W. Thornton, *Phil. Mag.*, 1925, [vi], **50**, 1135; *Ann. Report*, 1924, 11.
[11] *Phil. Mag.*, 1924, [vi], **47**, 337; *A.*, 1924, ii, 222.
[12] See also criticisms by J. Rice, *Trans. Faraday Soc.*, Oct., 1925; *A.*, ii, 1076 (part of a general discussion on photochemical reactions).
[13] *Loc. cit.*, Ref. 2.

as the original energy of activation. This high-energy product ("hot molecule") can then revert to normal by transfer of its excess energy to the reactant AB on collision, thus activating it, and so on. These reaction chains may be started by ordinary high-energy collisions. There is strong experimental evidence that such high-energy molecules can exist, and transfer their energy in this way.[14] The theory leads to velocity equations of the right form, *e.g.*, for a unimolecular reaction :—$-dC/dt = kC = AC^* = A(p^*/p)e^{-E/RT}C$, where C and C^* are the concentrations of the normal and activated reactants, respectively, p and p^* the corresponding *a priori* probabilities[15] of these states (p^*/p is not very different from unity), while A is the probability per second that an activated molecule will decompose ($1/A$, the mean life-period of the latter, is about 10^{-14} sec.). Although there is good evidence that molecular chain mechanisms actually occur in some reactions, difficulties arise which appear to rule this out as a *general* explanation.[16] Thus to keep a first-order course each decomposition must be immediately followed by activation of reactant in order to maintain the same statistical equilibrium $AB \rightleftharpoons (AB)^*$ as would obtain in the absence of reaction, which involves the highly improbable assumption that the "hot molecule," in spite of its numerous collisions with indifferent molecules, preserves its high energy content until it meets a reactant. The unimolecular rate of decomposition of nitrogen pentoxide is *not* influenced by diluents.[17] There is also the objection that decompositions are *endothermic*, so that supplementary activation would appear to be necessary; J. Rice [18] has, however, given reasons for doubting the validity of this criticism. No form of collision theory alone appears to be adequate in the case of unimolecular reactions.

The only alternative is activation by absorption of radiation present in temperature equilibrium with the system. The well-known Lewis-Perrin theory [19] of activation by selective absorption of radiation of frequency ν ($A + h\nu \rightarrow A^*$, and $E = Nh\nu$ per mol.)

[14] See, *e.g.*, O. Klein and S. Rosseland, *Z. Physik*, 1921, **4**, 46; *A.*, 1921, ii, 291; J. Franck, *ibid.*, 1921, **4**, 89; 1922, **9**, 259; *A.*, 1922, ii, 464; G. Cario and J. Franck, *ibid.*, 1922, **11**, 161; *A.*, 1922, ii, 809.

[15] "The *a priori* probabilities take account of the fact that each quantum state of definite energy content of a molecule may be realised in different ways, the p's representing the number of possible modes of realisation of each state" (A. C. McKeown, *Phil. Mag.*, 1923, [vi], **46**, 323).

[16] R. C. Tolman, ref. 6; M. Bodenstein, ref. 5; G. N. Lewis and D. F. Smith, ref. 7; J. Rice, ref. 12.

[17] See refs. 33.

[18] J. Rice, *loc. cit.*, ref. 12.

[19] *Trans. Faraday Soc.*, 1922, **17**: Discussion on the Radiation Theory of Chemical Action, p. 545 *et seq.* See also a review of radiation theories by H. S. Harned, *J. Franklin Inst.*, 1923, **196**, 181.

has been abandoned because the frequency predicted from the temperature coefficient of reaction velocity does not in general agree with absorption bands,[20] nor does it accelerate the reaction, and because activation by this means cannot occur with the speed required to account for known first-order rates.[21] R. C. Tolman's calculations [22] indicate, however, that this mechanism is a possible one for bimolecular reactions. Attempts to improve the radiation theory [23] found less favour than theories of collision, but on account of the difficulties of the latter, especially as regards unimolecular reactions, attention has again been focussed, by G. N. Lewis, R. C. Tolman, E. K. Rideal, J. Rice, and others, on radiation as the most probable activating agency. Tolman,[24] reviewing the various suggestions for a less restricted radiation theory, finds most promising the view that, on the assumption of a nearly continuous series of high energy quantum states corresponding to the idea of the weakening of a chemical bond, energy may be absorbed over a continuous range of frequencies, thus allowing an ample inflow. Somewhat similar ideas had been expressed by E. K. Rideal and W. C. McC. Lewis. G. N. Lewis and D. F. Smith,[25] who support a "general" radiation theory, employ the concept of discrete light quanta of relatively large size, thus facilitating collisional exchange of energy between molecules and quanta. J. Rice [26] has subjected these latter developments to a searching criticism, without, however, questioning the necessity of some form of radiation theory. These more recent views have not yet been formulated with sufficient precision for experimental test.

W. E. Garner [27] maintains that the close agreement between the critical increment from temperature coefficient with that calculated from the kinetic theory ($k = 2 \times$ total number of collisions $\times$ $e^{-E/RT}.P$), assuming $P = 1$, *i.e.*, every collision between activated molecules is "fruitful," cannot, as Hinshelwood [28] supposes, be accepted as evidence that P is unity, or that the critical increment from temperature coefficient is the true energy of activation.

[20] The interesting observation has been made by W. T. David, *Proc. Roy. Soc.*, 1925, *A*, **108**, 617; *A.*, ii, 980, that the rate of explosion of gas mixtures is increased when the infra-red radiation superimposed on that emitted by the burning gases is of the type that can be absorbed by the gases.

[21] J. A. Christiansen and H. A. Kramers, ref. 2; R. C. Tolman, ref. 6.

[22] Ref. 6.

[23] See ref. 19 and R. C. Tolman, *J. Amer. Chem. Soc.*, 1920, **42**, 2506; 1921, **43**, 269; *A.*, 1921, ii, 99, 248; J. Perrin, ref. 3.

[24] Refs. 6 and 23; J. Rice, ref. 12.

[25] Ref. 7. See also S. C. Roy, *Z. Physik*, 1925, **34**, 499; *A.*, ii, 1167.

[26] Ref. 12.

[27] *Phil. Mag.*, 1925, [vi], **49**, 463; **50**, 1031; *A.*, ii, 552, 1167.

[28] *Ibid.*, 1925, [vi], **50**, 360; *A.*, ii, 874.

M. Born and J. Franck [29] stress the importance of attacking problems of chemical kinetics from the point of view of the Bohr atom and the quantum laws of energy exchange. They consider that in the collision reaction $A + B \longrightarrow C^* \longrightarrow C + Q$ (heat of reaction), the fact that the primary complex, C*, formed at the moment of collision contains Q plus the relative kinetic energy, X, of A and B before collision does not of itself, as has often been assumed, prevent the formation of C, for molecules can exist temporarily having a *quantised* energy content much greater than Q. What does, however, prevent the formation of C is the infinitely small probability that $Q + X$ will agree with any quantum state (X being continuous). The energy of this incompletely quantised primary molecule (or " quasi-molecule ") can adjust itself to a discrete value neither by radiation nor conversion into translational energy, consequently C can be formed only if, during the period of collision, the complex is struck by a third atom or molecule, which carries off the excess energy (heat of reaction) as kinetic energy of translation, thereby converting C* into C. Such ternary collisions are evidently unnecessary in the reaction type $AB + C \longrightarrow AC + B$, since the continuous energy of translation is available for adjustment to a definite quantum state, and it is suggested that the catalytic effect of water vapour may be associated with a transition from the addition to the relatively faster exchange type of reaction. They are also unnecessary in the addition type when one reactant is large enough for the quantum states to be practically continuous. Surface catalysis provides an extreme example of the latter; when B strikes adsorbed A, energy adjustment to the appropriate quantum state can be established by the continuous energy reservoir of the solid catalyst. M. Polányi and E. Wigner,[30] while admitting the mechanism of ternary collision, differ from Born and Franck in regarding the probability of combination resulting from *binary* collision as finite, though small. M. Bodenstein [31] points out that the ternary collision theory suggests an acceleration of reaction in the presence of inert gases, which is not in accord with experiment.

Whilst the existence of homogeneous bimolecular gas reactions free from " wall effects " has been established, the fact that reputed examples of such unimolecular reactions have proved to be not independent of surface/volume ratio or of pressure has led to serious doubts as to their actual existence. Thus the best defined example, that of the thermal decomposition of nitrogen pentoxide, was

[29] *Z. Physik*, 1925, **31**, 411; *A.*, ii, 266; *Ann. Physik*, 1925, [iv], **76**, 225; *A.*, ii, 365; J. Franck, *Z. Elektrochem.*, 1925, **31**, 350; *Naturwiss.*, 1924, **47**, 1063; *A.*, 1925, ii, 836.

[30] *Z. Physik*, 1925, **33**, 429.

[31] Ref. 5.

apparently catalysed by nitrogen peroxide.[32] In view of its great theoretical importance, this reaction has been carefully re-examined by four independent investigators,[33] who agree in finding no evidence of catalysis or wall-effect and no variation of rate (*a*) over an enormous range of pressure down to less than 1 mm., (*b*) in the presence of excess of argon, air, and nitrogen peroxide. Further, the rate is much the same in inert solvents over wide concentration ranges.[34] The absence of any retarding influence of diluents or of very low pressures renders improbable any chain mechanism. According to H. S. Hirst and E. K. Rideal,[35] however, who worked at pressures down to 0·01 mm., the rate, constant above 0·25 mm., begins to *increase* at this critical pressure, approaching a limiting value five times the normal as the pressure diminishes. This limiting value is in remarkably close agreement with the Dushman-Rideal [36] equation :—$dC/dt = \nu e^{-Nh\nu/RT}.C$, which suggests some form of radiation mechanism of activation. The reaction is considered to take the following course : one-fifth of the activated molecules always decompose independently of pressure, whilst four-fifths decompose only if, after activation, they fail to collide during a period of about 10^{-6} second (collision within this period causes simple de-activation). There seems to be no reason for doubting the unimolecular homogeneous character of this reaction.

D. F. Smith [37] finds that the thermal decomposition of sulphuryl chloride, which has been stated [38] to be a wall reaction, is a first-order reaction independent of surface/volume ratio except to a slight extent at lower temperatures. According to D. L. Watson,[39] the thermal decomposition of four derivatives of oxalacetic ester in the pure liquid phase follows a unimolecular course, and inert solvents are without influence on the velocity coefficients. The phenyl derivative decomposes autocatalytically. It is shown that, by molecular chain activation, first-order reactions should be auto-

[32] F. Daniels and E. H. Johnston, *J. Amer. Chem. Soc.*, 1921, **43**, 53; *A.*, 1921, ii, 249; R. H. Lueck, *ibid.*, 1922, **44**, 757; *A.*, 1922, ii, 433; F. Daniels, O. R. Wulf, and S. Karrer, *ibid.*, 1922, **44**, 2402; *A.*, 1923, ii, 24.

[33] J. K. Hunt and F. Daniels, *ibid.*, 1925, **47**, 1602; *A.*, ii, 801; E. C. White and R. C. Tolman, *ibid.*, 1925, **47**, 1240; *A.*, ii, 682; H. S. Hirst, *J.*, 1925, **127**, 657; H. S. Hirst and E. K. Rideal, *Proc. Roy. Soc.*, 1925, *A*, **109**, 526.

[34] R. H. Lueck, ref. 32.

[35] Ref. 33.

[36] S. Dushman, *J. Amer. Chem. Soc.*, 1921, **43**, 397; *A.*, 1921, ii, 315; E. K. Rideal, *Phil. Mag.*, 1920, [vi], **40**, 461; *A.*, 1920, ii, 676; J. Rice, *ibid.*, 1923, [vi], **46**, 312; *A.*, 1923, ii, 622; A. McKeown, *ibid.*, 1923, [vi], **46**, 321; *A.*, 1923, ii, 623.

[37] *J. Amer. Chem. Soc.*, 1925, **47**, 1862; *A.*, ii, 876.

[38] C. N. Hinshelwood and C. R. Prichard, *J.*, 1923, **123**, 2725.

[39] *Proc. Roy. Soc.*, 1925, *A*, **108**, 132; *A.*, ii, 556. For similar reactions, see C. N. Hinshelwood, *J.*, 1920, **117**, 156; 1921, **119**, 721.

catalytic, and this is considered to be the essential character of all four reactions. The thermal decomposition of ozone [40] is mainly homogeneous (second order), but not free from wall effect. Oxygen retards and indifferent gases accelerate the reaction. The mechanism proposed is: $O_3 \rightleftharpoons O_3^*$; $O_3^* + O_3 \rightleftharpoons$ Complex; Complex $\longrightarrow 3O_2$, it being assumed that the complex may break up into O_2 or O_3 either spontaneously or on collision; collision with oxygen favours Complex $\longrightarrow O_3$, and collision with an indifferent gas favours Complex $\longrightarrow O_2$. This mechanism includes the possibility of molecular chain activation and Born-Franck ternary collisions.

Theories which provide for energy transfer adequate to maintain known reaction rates touch but one aspect of the question. The energy of collision in gases dried to inertness is presumably not altered in the presence of minute traces of water, and in this sense most reactions are catalytic. This point has been emphasised by R. G. W. Norrish,[41] who considers that the inert "dry molecules" are partly activated by close association with water, which, in virtue of its high polarity, weakens the structure of the "resting" molecule, so that the supplementary activation necessary for reaction may be attained by collision. The catalytic activity of surfaces is due to similar causes, non-polar surfaces such as paraffin wax being non-catalytic. The rate of photochemical union of hydrogen and chlorine is independent of the pressure of water vapour down to 10^{-4} mm., when it begins to fall, reaching zero at 10^{-7} mm. water-vapour pressure.[42] This corresponds to a gradual removal of the water film. It is therefore suggested that the removal of this catalytically active film rather than "ultra-dryness" of the gases is responsible for the suspension of reactions of dry gases in general. Quantitative studies of moisture effect on reaction rate are much needed.

Heterogeneous Catalysis and Adsorption.

A very considerable amount of work on this subject has been done since it was last noticed in these Reports.[43] I. Langmuir's well-known theory [43] has on the whole been substantiated and is

[40] R. O. Griffiths and A. McKeown, *J.*, 1925, **127**, 2086.

[41] *J.*, 1923, **123**, 3006; H. S. Taylor, *J. Physical Chem.*, 1924, **28**, 897.

[42] M. Bodenstein and W. Dux, *Z. physikal. Chem.*, 1913, **85**, 297; *A.*, 1913, ii, 1039; A. Coehn and G. Jung, *ibid.*, 1924, **110**, 705; *A.*, 1925, ii, 142; R. G. W. Norrish, *J.*, 1925, **127**, 2316; *A.*, ii, 1179; *Trans. Faraday Soc.*, Oct., 1925; *A.*, ii, 1080.

[43] See the Reports of the Committee on Contact Catalysis (National Research Council), especially the second report: W. D. Bancroft, *J. Physical Chem.*, 1923, **27**, 801; and third report: H. S. Taylor, *ibid.*, 1924, **28**, 898. An excellent account is given by H. S. Taylor in his "Text-book of Physical Chemistry" (Macmillan, 1924). See also the discussion on catalysis, *J. Faraday Soc.*, 1922, **17**, 607.

very generally accepted. A consideration of kinetic studies, of the parallel investigation of adsorptive capacity and reaction rate for the same catalyst, and of work on catalyst surfaces has, however, led H. S. Taylor [44] to a "concept of the catalytic surface which is, perhaps, more comprehensive than earlier efforts and which leads to interesting general conclusions with reference to matter in the solid state." It has been fully established that the Langmuir active areas or centres occupy only a small fraction of the surface, that they vary in their capacity both to adsorb and promote reaction, and that metallic catalysts are extraordinarily sensitive to heat treatment and poisoning, but the consequent reduction of catalytic activity greatly exceeds that of adsorptive capacity. To account for these facts, a modification of the Langmuir concept is proposed, and illustrated by reference to a metallic catalyst such as nickel. Whilst giving no information about the surface, *X*-ray examination [45] shows that active catalysts prepared by low-temperature reduction of oxides consist of fine granules having the definite lattice structure of the crystals. The mode of production and sensitivity to moderate heat treatment (incipient sintering) suggest incomplete surface crystallisation, *i.e.*, occasional groups of atoms fixed in metastable positions associated with high energy and chemical unsaturation relative to the atoms in the regular lattice below (Fig. 1).[46]

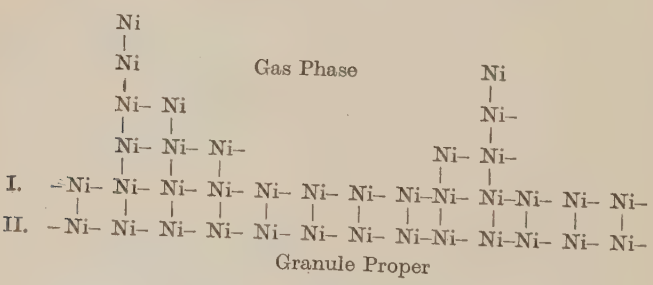


Fig. 1.

From layer II (where each Ni is surrounded by six others) outwards, the degree of constraint or saturation decreases to a varying extent, the "peak" atoms differing from gaseous atoms only by the single valence which holds them to the solid. While a free atom can bind four CO groups, a singly anchored atom may adsorb three such groups (or their equivalent), and a doubly anchored, two. Corner and edge atoms of a crystal are also unsaturated to

[44] *Proc. Roy. Soc.*, 1925, *A*, **108**, 105; *A.*, ii, 562.

[45] G. L. Clark, W. C. Asbury, and R. M. Wick, *J. Amer. Chem. Soc.*, 1925, **47**, 2661; R. W. G. Wyckoff and E. D. Crittenden, *ibid.*, p. 2866.

[46] Figure taken from H. S. Taylor; ref. 44.

different extents. Reactants such as hydrogen and ethylene may be held by the same Ni atom (Langmuir postulated adsorption of reactants on *adjacent* centres). The rise of activity of platinum and silver in oxidation catalysis is due to surface disintegration leading to an increased number of unsaturated atoms. Moderate heat treatment causes atomic displacement to a more regular surface with loss of energy, the more mobile singly-bound and highly active atoms being the more readily displaced. That the saturation capacity of a surface varies for different adsorbed gases is thus to be expected; there are, for example,[47] more copper atoms capable of holding carbon monoxide than hydrogen. At higher temperatures, adsorption is increasingly confined to the more unsaturated surface atoms and it is to these that poisons first become attached.[48] Correlating the adsorptive and catalytic power of copper for the reaction $C_2H_4 + H_2 = C_2H_6$, R. N. Pease[49] found that poisoning by mercury, whilst not appreciably affecting the weaker (high pressure) adsorption, destroyed both the stronger (low pressure) adsorption and the catalytic activity, and a copper catalyst which strongly adsorbed 5 c.c. of carbon monoxide suffered a 90% loss of catalytic activity by adsorbing only 0·05 c.c. of this poison, which means that the surface owed 90% of its activity to less than 1% of its strongly adsorbing centres.[50] Thus even low-pressure adsorption measurements may give no true index of catalytic activity. That the varying degree of saturation of surface atoms involves varying catalytic activity is well illustrated by the progressive poisoning experiments of G. Vavon and A. Husson,[51] who found that when platinum had been poisoned by carbon disulphide just sufficiently to suppress the hydrogenation of dipropyl ketone, it could still hydrogenate piperonal and nitrobenzene, whilst a further dose of poison stopped the former, but not the latter reaction, which again could be poisoned by more carbon disulphide. The amount of active surface is thus determined by the reaction catalysed.

Support for the theory outlined above is found in the high values of heats of adsorption, *e.g.*, of hydrogen on nickel[52]: 13,500—20,500

[47] R. N. Pease, *J. Amer. Chem. Soc.*, 1923, **45**, 1196, 2235; *A.*, 1923, ii, 472, 842.

[48] See, *e.g.*, data for hydrogen on nickel: A. W. Gauger and H. S. Taylor, *ibid.*, p. 920; *A.*, 1923, ii, 398.

[49] R. N. Pease, *ibid.*, p. 2296; *A.*, 1923, ii, 862.

[50] R. N. Pease and L. Stewart, *ibid.*, 1925, **47**, 1235; *A.*, ii, 691; see also E. B. Maxted, *Trans. Faraday Soc.*, 1917, **13**, 36; E. F. Armstrong and T. P. Hilditch, *ibid.*, 1922, 17, 669.

[51] *Compt. rend.*, 1922, **175**, 277; *A.*, 1922, ii, 631.

[52] R. A. Beebe and H. S. Taylor, *J. Amer. Chem. Soc.*, 1924, **46**, 43; *A.*, 1924, ii, 159; B. Foresti, *Gazzetta*, 1923, **53**, 487; 1924, **54**, 132; 1925, **55**, 185; *A.*, 1923, ii, 747; 1924, ii, 320; 1925, ii, 692.

cal. per mol., depending on its history. E. A. Blench and W. E. Garner [53] find values for oxygen on charcoal varying from 60,000 cal., at low temperatures and high adsorptions, to the surprisingly high value of 220,000 cal. at high temperatures and low adsorptions. As expected, there is a greater heat effect for initial than for subsequent adsorption. The heat of formation of carbon dioxide from solid charcoal, which includes the endothermal breaking of carbon linkings, is 97,000 cal., whilst from gaseous carbon it is 380,000 cal.[54] The high heat of adsorption indicates that some carbon links on the surface are already broken, yielding atoms in a highly unsaturated and active state, so that their combustion resembles that of gaseous rather than of crystalline carbon. The fact that the heat of combustion of the incompletely crystallised charcoal exceeds that of graphite is also in agreement with the theory. E. F. Armstrong and T. P. Hilditch,[55] who have made a thorough study of catalytic hydrogenation at nickel surfaces, express general agreement with this theory, but consider that the acting nickel atom may at the moment of catalytic change be actually detached from the metal as a complex of nickel, oil, and hydrogen, which breaks up with deposition of the nickel. According to A. W. Gauger,[56] pure nickel and platinum distilled in a vacuum on to the surface of glass wool are catalytically inactive, so that activity depends on condition rather than on extent of surface. He regards the molecules or atoms at active centres as having electrons in energy levels higher than normal. M. Bodenstein [57] refers to deformation of such adsorbed molecules.

Special interest attaches to the investigations of W. G. Palmer [58] and F. H. Constable [59] dealing mainly with the catalytic dehydrogenation of alcohols (vapour) in the presence of copper. The reaction rate is independent of pressure over a 12-fold range, showing that reaction occurs only in the layer in immediate contact with the copper. The primary alcohols, ethyl, propyl, butyl, *iso*butyl, and *iso*amyl, decompose at the same rate (*iso*propyl

[53] *J.*, 1924, **125**, 1288; *Nature*, 1924, **114**, 932; *A.*, 1925, ii, 140.
[54] K. Fajans, *Ver. Deut. Physikal. Ges.*, 1912, **14**, 324.
[55] *Proc. Roy. Soc.*, 1925, *A*, **108**, 111; *A.*, ii, 562.
[56] *J. Amer. Chem. Soc.*, 1925, **47**, 2278; *A.*, ii, 1072.
[57] *Annalen*, 1924, **440**, 177; *A.*, 1925, ii, 216.
[58] W. G. Palmer, *Proc. Roy. Soc.*, 1920, *A*, **98**, 13; 1921, *A*, **99**, 412; *A.*, 1920, ii, 609; 1921, ii, 542; D. M. Palmer and W. G. Palmer, *ibid.*, p. 402; *A.*, 1921, ii, 541; W. G. Palmer, *ibid.*, 1922, *A*, **101**, 175; *A.*, 1922, ii, 437; W. G. Palmer and F. H. Constable, *ibid.*, 1924, *A*, **106**, 250; 1925, *A*, **107**, 255; *A.*, 1924, ii, 843; 1925, ii, 311.
[59] F. H. Constable, *ibid.*, pp. 270, 279; *A.*, ii, 311; *Nature*, 1925, **116**, 278; *A.*, ii, 983; *Proc. Roy. Soc.*, 1925, *A*, **108**, 355; *A.*, ii, 804; *Proc. Camb. Phil. Soc.*, 1925, **22**, 738; *A.*, ii, 881.

alcohol five times faster) and with the same temperature coefficient, indicating identical mechanism and energy relations. The adsorbed molecules are oriented with the hydroxyl group only in close association with the surface. At the active centres the OH group is distorted so that the hydrogen atom readily oscillates to the copper, a second atom of hydrogen of the $-CH_2 \cdot OH$ group breaking away automatically with formation of aldehyde. The energy of activation is supposed to be concentrated in the hydrogen atom of the OH group. The catalyst, prepared by successive oxidation and reduction at low temperature, is perfectly reproducible and a detailed study leads to views concerning the nature of the surface which differ in no essential respect from those of H. S. Taylor. The active centres form only a very small fraction of the total surface. They are associated with varying critical increments, most of the reaction occurring at the centres of low increment. A mathematical analysis of the process is given.

The varying catalytic and adsorptive activity of different portions of a charcoal surface has been studied by E. K. Rideal and W. M. Wright,[60] who express views in close agreement with those of Taylor and Constable. By measuring the rate of absorption of oxygen and evolution of carbon dioxide by charcoal suspended in water (a zero-order reaction), they find the active fraction of the surface to be 0·38%, this being the ratio of the number of molecules of poison just sufficient to stop the reaction to the number necessary to saturate the surface. In the catalytic oxidation of organic acids, 40% of the surface is active.

Much discussion has centred round the question as to whether the active substance in a metal catalyst is the metal or an oxide. Thus M. C. Boswell [61] and his associates maintain that the incompletely removed oxygen in nickel granules is vital for their activity. Recent work [62] appears, however, to have proved conclusively that the active substance is nickel.

It is unlikely that the complex phenomena of promoter action will be explicable by any one theory. W. W. Hurst and E. K. Rideal [63] ascribe the promoting action of palladium on copper to interface effects, the molecules at the boundary between two solid phases being in a specially active condition. The promoting action of irreducible oxides on nickel in the reaction $CO_2 + 4H_2 = CH_4 +$

[60] *J.*, 1925, **127**, 1347.

[61] See H. S. Taylor, Report on Contact Catalysis, ref. 43; M. C. Boswell and C. H. Bayley, *J. Physical Chem.*, 1925, **29**, 11; *A.*, ii, 215.

[62] A. W. Gauger, *J. Amer. Chem. Soc.*, 1925, **47**, 2278; *A.*, ii, 1072; H. Adkins and W. A. Lazier, *ibid.*, 1924, **46**, 2291; *A.*, 1924, i, 1278; C. Kelber, *Ber.*, 1924, **57**, [*B*], 136, 142; *A.*, 1924, ii, 243, 244.

[63] *J.*, 1924, **125**, 685, 694.

$2H_2O$ is attributed by S. Medsforth [64] to dehydration or decomposition of intermediate compounds, and to selective adsorption. E. F. Armstrong and T. P. Hilditch [65] consider the effect mainly due to an increase of surface. W. W. Russell and H. S. Taylor [66] find no proportionate increase of adsorption with catalytic activity of nickel when promoted by thoria, so that the effect is to render the surface more active rather than more extensive. In conformity with Taylor's theory of the catalytic surface, an irreducible oxide prevents coalescence (sintering) of the nickel atoms, its chief function being thus to produce a larger number of unsaturated atoms of high activity. R. W. G. Wyckoff,[67] by an *X*-ray examination of ammonia–iron catalysts promoted by potash and alumina, finds that the latter prevent the growth of the iron crystals.

W. A. Bone and G. W. Andrew [68] have investigated the catalytic oxidation of carbon monoxide at a gold surface at 300°. The theoretical mixture $2CO + O_2$ reacts at a rate proportional to its pressure when the catalyst has reached its normal activity by continued reaction. This normal activity is strongly stimulated by previous exposure to either reactant or by reaction in a mixture containing excess of either reactant, and greatly reduced by keeping at room temperature or at 300° in a vacuum. After such alterations it reverts to its normal activity on continued reaction in the theoretical mixture. They consider, therefore, that whilst both gases are "activated" by association with the surface, such activation is by no means strictly confined to the surface layer, but extends to the more deeply "occluded" gases. This is of considerable interest in view of the general conviction that surface catalysis is determined by a single adsorbed layer.

C. N. Hinshelwood [69] and his associates have investigated the influence of catalytic surfaces (heated wires) on gas reactions which are bimolecular in the homogeneous phase. If the active surface of the catalyst remains saturated with adsorbed molecules, the reaction rate is independent of pressure (zero order), and no conclusion can be drawn as to the number of molecules involved in the catalytic reaction. With small adsorption, however, this number is given by the order of reaction measured in the usual way. Intermediate states give illusory results. Zero orders are given by

[64] *J.*, 1923, **123**, 1452.
[65] *Proc. Roy. Soc.*, 1923, *A*, **103**, 586; *A.*, 1923, ii, 551.
[66] *J. Physical Chem.*, 1925, **29**, 1325.
[67] *Loc. cit.*, ref. 45.
[68] *Proc. Roy. Soc.*, 1925, *A*, **109**, 459.
[69] C. N. Hinshelwood and C. R. Prichard, *Proc. Roy. Soc.*, 1925, *A*, **108**, 211; *A.*, ii, 567; *J.*, 1925, **127**, 327, 1552; C. N. Hinshelwood and R. E. Burk, *ibid.*, pp. 1105, 2896.

$NH_3|W$ and $HI|Au$; first orders by $N_2O|Au$, $N_2O|Pt$, $HI|Pt$, $NH_3|Pt$, $NH_3|SiO_2$. The catalyst promotes rapid first-order reaction, *e.g.*, of $N_2O = N_2 + O$, by "accepting" oxygen atoms which then evaporate as molecules. It also accelerates reaction by lowering the energy of activation,[70] which (calculated in the usual way) is frequently about half the bimolecular value. There is no justification, however, for attaching any important significance to the ratio 2 : 1. A similar ratio is obtained by H. A. Taylor [71] for the decomposition of hydrogen iodide at glass walls and in the homogeneous phase. Kinetic studies of the reduction of carbon dioxide by hydrogen at the surface of hot platinum and tungsten wires by C. N. Hinshelwood and C. R. Prichard [72] lend strong support to the theory of H. S. Taylor.

The activating effect of a polar surface has been strikingly demonstrated by R. G. W. Norrish.[73] Both dry chlorine and bromine react with ethylene rapidly on glass, still more rapidly on stearic acid, and scarcely at all on paraffin wax. This is regarded as strong evidence that molecular activation depends on induced polarity by association with a polar molecule. This reaction has been employed as a measure of the polarity of various surfaces.[74]

The Surfaces of Liquids.

According to the Langmuir-Harkins theory of the oriented unimolecular layer, which has been so firmly established as regards long-chain substances with a polar end-group on water, where surface concentration and pressure can be *directly* measured, the excess surface concentration of a solution is similarly restricted to a unimolecular layer, and the surface tension of the solution is due only to the stray fields of force of the molecules in this layer. The latter state is obviously less simple than the former,[75] and recent work [76] suggests that the phenomena at the surfaces of solutions cannot always be interpreted in quite such a simple manner. In the absence of trustworthy direct methods of measuring surface concentration, Γ, it has generally been calculated from the surface tension, σ, of a solution of concentration C by the Gibbs equation: $\Gamma = -C/RT \cdot d\sigma/dC$, a form which is valid only for ideal solutions. The area, A, per molecule in the layer, obtained by assuming it to be unimolecular, is generally in sufficiently good agreement with

[70] See also C. N. Hinshelwood and B. Topley, *J.*, 1923, **123**, 1014.
[71] *J. Physical Chem.*, 1924, **28**, 984; *A.*, 1924, ii, 745.
[72] *J.*, 1925, **127**, 806, 1546.
[73] *J.*, 1923, **123**, 3006; 1925, **127**, 2318; 1926, 55.
[74] N. K. Adam, R. S. Morrell, and R. G. W. Norrish, *J.*, 1925, **127**, 2793.
[75] F. G. Donnan, *Brit. Assoc. Rep.*, 1923, 59.
[76] See, *e.g.*, S. Sugden, *J.*, 1924, **125**, 1167; *Ann. Report*, 1924, p. 8.

expected values to confirm the theory, but conclusions as to the state of the surface molecules based on these values of A are not always so certain as in the case of insoluble films. Recent measurements indicate that the acetic acid molecule occupies 28% more area at an air–water than at a hydrocarbon–water interface,[77] and that whilst pyrogallol (air–water) occupies only 16% more area than phenol, which stands vertical, the *o*- and *m*-dihydroxy-derivatives must be considerably inclined to, and the *p*-derivative flat on the surface, giving incompressible although not close-packed films.[78]

In recent work the importance of employing the Gibbs equation in its exact form has been emphasised, and activities have been used instead of concentrations. Except for very dilute solutions of non-electrolytes, the concentration formula gives quite erroneous results. A. K. Goard and E. K. Rideal [79] find that with increasing activity of phenol in aqueous salt solution (due to increase of salt as well as phenol concentration) the adsorption increases to a maximum, leading to values of A and of surface thickness in excellent agreement with accepted values of the dimensions of the benzene nucleus. The adsorbed phenol is thus contained in a single layer of close-packed, vertical molecules. Although this film is probably the chief factor in determining the surface tension, the latter is definitely influenced through the film by molecules below it, indicating (contrary to the Langmuir-Harkins theory) the operation of forces exceeding molecular dimensions. The work of T. Iredale [80] and others points in the same direction, while E. Edser [81] considers that attractive forces may be appreciable over a range of many molecular diameters from the surface. The foundation of the film as well as the film itself cannot be neglected in a complete theory of surface tension.

Salt solutions having a higher surface tension than water are covered, according to Langmuir, with a single layer of oriented water molecules. According to recent measurements [82] on such solutions, based on the Gibbs equation (activities), the apparent thickness of this layer decreases considerably with increasing concentration, the effect depending on the nature of the salt. This is difficult to reconcile with the single layer theory. Various suggestions are made, *e.g.*, that the increasing diffusion pressure of

[77] W. D. Harkins and H. M. McLaughlin, *J. Amer. Chem. Soc.*, 1925, **47**, 1610; *A.*, ii, 771.

[78] W. D. Harkins and E. H. Grafton, *ibid.*, p. 1329; *A.*, ii, 658.

[79] *J.*, 1925, **127**, 1668.

[80] *Phil. Mag.*, 1923, [vi], **45**, 1088; 1924, **48**, 177; 1925, **49**, 603; *A.*, 1923, ii, 379; 1924, ii, 663; 1925, ii, 508.

[81] Brit. Assoc. Fourth Report on Colloid Chemistry, 1922, p. 40.

[82] A. K. Goard and E. K. Rideal, *J.*, 1925, **127**, 1668; W. D. Harkins and H. M. Mc Laughlin, *J. Amer. Chem. Soc.*, 1925, **47**, 2083; *A.*, ii, 959.

the ions forces them nearer the surface and thus perhaps modifies the orientation of the water molecules, and that the water shell of the ions becomes smaller or more tightly packed with increasing concentration.

The equation of state proposed by Langmuir [83] (following J. Traube) [84] for the "Gibbs layer" is $FA = RT$, where F, the surface pressure, is the excess surface tension of the solvent over that of the solution, and A is the area occupied by a gram-molecule as surface excess. This two-dimensional analogue of the ideal gas law, whilst approximately valid for low values, fails at high values of F, suggesting a behaviour similar to that of compressed gases. R. K. Schofield and E. K. Rideal,[85] using the Gibbs formula (activities), find that for aqueous ethyl alcohol, with increasing concentration, A first diminishes to a minimum, which is only slightly larger than the value corresponding to a close-packed film, then rises to a steady value three times the minimum for some reason not fully explained. Pyridine at a water–mercury interface shows similar behaviour. When, for aqueous solutions of fatty acids, C_4 to C_{12}, at benzene–water as well as air–water interfaces, FA/RT is plotted against F, curves strongly resembling the corresponding ones for highly compressed gases are obtained, leading to $F(A - B) = xRT$ as the equation of state of the surface layer for high values of F. B (compare b of the gas equation) is the minimum area of an adsorbed gram-molecule under high surface compression, and $1/x$ represents the lateral molecular cohesion, which increases with length of the carbon chain. This cohesion is greatly reduced when the chains are in a hydrocarbon phase. For sucrose at a water–mercury interface, $x = 1$ (no cohesion), giving the exact analogue of the Sackur osmotic pressure equation $P(V - b) = RT$, and the value of B, which is in striking agreement with the dimensions of the molecule from other sources, indicates that its long axis lies in the plane of the interface. The general conclusion is reached that the molecules adsorbed in a unimolecular layer from a weak solution affect the surface tension only by their thermal agitation. "At a given temperature their effectiveness depends solely on their surface concentration, interfacial areas, and lateral cohesion." M. Volmer and P. Mahnert,[86] from *direct* measurements of the amount of benzophenone adsorbed from a crystal on the surface of mercury, obtain the same equation of state. It has also been deduced theoretically by S. C. Kar.[87]

[83] *J. Amer. Chem. Soc.*, 1917, **39**, 1848; *A.*, 1917, ii, 525.
[84] *Annalen*, 1891, **265**, 27; *A.*, 1891, 1468.
[85] *Proc. Roy. Soc.*, 1925, *A*, **109**, 57; *A.*, ii, 960; *Nature*, 1925, **116**, 886.
[86] *Z. physikal. Chem.*, 1925, **115**, 239; *A.*, ii, 508.
[87] *Physikal. Z.*, 1925, **26**, 615; *A.*, ii, 1045.

An equation of this kind had previously been shown by N. K. Adam [88] to represent the behaviour of expanded films of insoluble fatty acids.

Organic vapours are reversibly adsorbed on mercury surfaces, giving, according to T. Iredale,[89] unimolecular films. The considerable drop of surface tension caused by condensation from a nearly saturated vapour indicates that the interfacial tension between two liquids is not due exclusively to the arrangement of a single layer of molecules, but results from attractions extending through a layer many molecules thick. Iredale's mode of using the drop-weight method has been adopted by others [90] as being more rational than that of J. L. R. Morgan and W. D. Harkins.

The continued study of long-chain surface films by N. K. Adam [91] has shown that methyl esters of the alcohols do not form stable films, the methyl radical destroying the anchorage of the polar group on water, and that with sufficient complexity of the molecular heads (*e.g.*, the substituted ureas), a "two-dimensional allotropy" occurs, depending on different types of packing in the film, and associated with a definite transition temperature. Pentaerythritol tetrapalmitate exists as a stable film with its four long chains parallel and perpendicular to the surface.

A. P. Cary and E. K. Rideal,[92] by placing crystals or lenses of long-chain fatty acids and esters (instead of the usual solution in a volatile solvent) on the surface of water, find that surface solution occurs, not by bulk spreading, but from the edge of contact of the lens or crystal,[93] and at a measurable rate until kinetic equilibrium is reached between the substance and the film. The process is reversible and occurs in two stages, first the production of an expanded film under zero compression, $F = \sigma_{\text{water}} - \sigma_{\text{film}}$; secondly, its condensation to an equilibrium pressure, F_e, characteristic of the substance. The system is then the two-dimensional analogue of a saturated solution in equilibrium with the solid solute. Contrary to the conclusions of A. Marcelin,[94] there is a

[88] *Proc. Roy. Soc.*, 1922, *A*, **101**, 516; *A.*, 1922, ii, 687; *Ann. Report*, 1923, p. 22.

[89] Ref. 80.

[90] See A. K. Goard and E. K. Rideal, *J.*, 1925, **127**, 780.

[91] Summarising paper: *J. Physical Chem.*, 1925, **29**, 87; *A.*, ii, 195; N. K. Adam and J. W. W. Dyer, *Proc. Roy. Soc.*, 1924, *A*, **106**, 694; *A.*, 1925, ii, 32.

[92] *Proc. Roy. Soc.*, 1925, *A*, **109**, 301, 318, 331; *A.*, ii, 1046—1048; *Nature*, 1925, **115**, 457; *A.*, ii, 388.

[93] M. Volmer and P. Mahnert, *loc. cit.*, find that benzophenone spreads from a crystal placed on mercury *directly*, and not by vaporisation or bulk solution.

[94] *Compt. rend.*, 1921, **173**, 38; *A.*, 1921, ii, 488.

limit to the expansibility of the film due to the mutual attraction of the carbon chains. With increasing temperature dF_e/dT has a constant positive value through a considerable range, including that over which the film changes from the condensed to the expanded state. At the melting point of the crystal it changes sharply, becoming in some cases zero, in others negative, and finally after a transition point less negative. The curves for different substances are straight lines, generally parallel. The breaks are attributed to expansion of the lens–water interfacial film. Film expansion is regarded as due to hydration of the polar heads, this effect being opposed by attraction of the hydrocarbon chains for each other. An application of the Clapeyron equation to the two-dimensional system gives the latent heats of the changes, including approximately correct values of the latent heats of fusion of the crystals.

The question of the rate of evaporation of water through a film of insoluble fatty acid has been discussed. The conclusion of G. Hedestrand [95] that such a film has no retarding effect has been refuted by N. K. Adam [96] and by E. K. Rideal,[97] who has shown experimentally that considerable retardation occurs, the effect being increased by an increase in surface concentration.

Sir William Hardy,[98] in a lecture to the Chemical Society, has discussed the problems of interfaces. His well-known work on lubrication leads to the view that the surface forces responsible for the primary unimolecular layer of oriented molecules on a solid, although acting directly over ranges comparable with molecular dimensions, are nevertheless by some means transmitted over much greater distances through secondary films, which, possibly on account of induced polarity, themselves are structured to a gradually decreasing extent owing to the operation of thermal agitation. The essential differences between primary and secondary layers, and the factors governing their formation have been summarised by Cary and Rideal.[99]

Strong Electrolytes.

Previous Reports have indicated that in recent years the attempt to interpret the properties of solutions of strong electrolytes in terms of a degree of dissociation measured by the conductivity ratio has been abandoned. Instead much effort is being devoted to the exact determination of the thermodynamical properties of

[95] *J. Physical Chem.*, 1924, **28**, 1245; *A.*, 1925, ii, 102.
[96] *Ibid.*, 1925, **29**, 610; *A.*, ii, 658.
[97] *Ibid.*, 1925, **29**, 1585.
[98] *J.*, 1925, **127**, 1207; Brit. Assoc. Fourth Report on Colloid Chemistry, 1922, 185.
[99] *Loc. cit.*, ref. 92, p. 301.

solutions, and for their expression the activity concept of G. N. Lewis [1] has been almost universally adopted.

It may perhaps be emphasised here that activities are not, as they have been often regarded, empirical quantities which must be inserted into the theoretical equations in place of concentrations, in order to produce the observed results. They are in fact exact expressions of the partial free energies of substances in solution. If ΔF is the free energy change (per mol.) in the transfer of a substance from a solution in which its concentration is c to a second solution in which its concentration is c_0, then the ratio of the corresponding activities is given by $\Delta F = RT \log_e \alpha/\alpha_0$. If the solution were "ideal," the free energy change in the transfer would be $\Delta F = RT \log_e c/c_0$. Now if the second solution be that which has been chosen as standard (usually an infinitely dilute solution), we may put $\alpha_0 = c_0$, since only the *ratio* of the activities has been defined. It is now evident that α/c, which is known as the activity coefficient f, is a measure of the deviation from the ideal relation.

A number of important measurements of activities have appeared during the year, among which the following may be mentioned: sodium hydroxide in aqueous solution,[2] sodium hydroxide in sodium chloride solutions,[3] potassium hydroxide in potassium chloride solutions,[4] water in sodium chloride and potassium chloride solutions,[5] sulphuric acid in aqueous sulphate solutions,[6] hydrogen chloride in ethyl-alcoholic solution,[7] hydrogen chloride in methyl-alcoholic solution,[8] calcium, strontium, and barium chlorides in aqueous solution,[9] barium chloride in aqueous solution,[10] hydrogen fluoride in aqueous solution.[11] G. Scatchard has redetermined the activities of hydrogen chloride in aqueous solution [12] and has recalculated the activities of potassium, sodium and lithium chlor-

[1] G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw, Hill Book Co., 1923. Compare also H. S. Harned in "A Treatise on Physical Chemistry," edited by H. S. Taylor (Macmillan, 1924), p. 701.

[2] H. S. Harned, *J. Amer. Chem. Soc.*, 1925, **47**, 676; *A.*, ii, 397.

[3] *Idem, ibid.*, p. 684; *A.*, ii, 398.

[4] *Idem, ibid.*, p. 689; *A.*, ii, 398.

[5] *Idem, ibid.*, p. 930; *A.*, ii, 538.

[6] H. S. Harned and R. D. Sturgis, *ibid.*, p. 945; *A.*, ii, 538.

[7] H. S. Harned and M. H. Fleysher, *ibid.*, p. 82; *A.*, ii, 538. Many of the results in refs. 2 to 7 are collected in a summarising paper by H. S. Harned, *Z. physikal. Chem.*, 1925, **117**, 1; *A.*, ii, 977.

[8] G. Nonhebel and H. Hartley, *Phil. Mag.*, 1925, [vi], **50**, 729; *A.*, ii, 1061.

[9] W. W. Lucasse, *J. Amer. Chem. Soc.*, 1925, **47**, 743; *A.*, ii, 399.

[10] J. N. Pearce and R. W. Gelbach, *J. Physical Chem.*, 1925, **29**, 1023; *A.*, ii, 867.

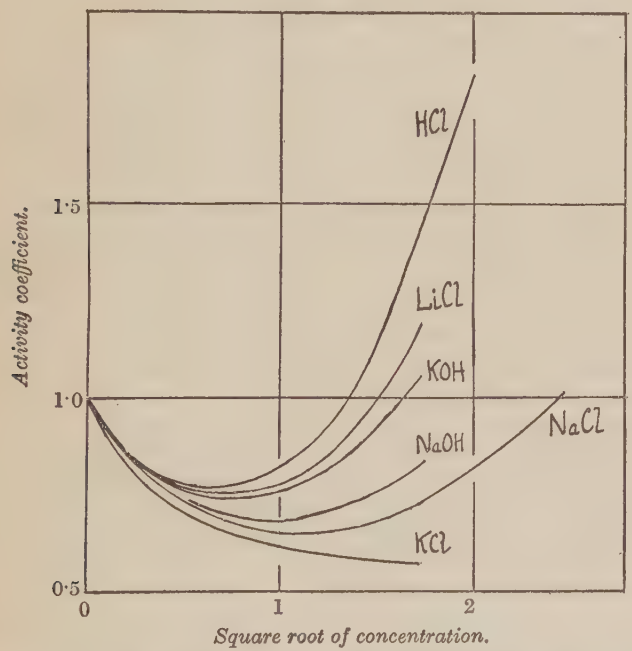
[11] J. D. C. Anthony and L. J. Hudleston, *J.*, 1925, **127**, 1122.

[12] *J. Amer. Chem. Soc.*, 1925, **47**, 641; *A.*, ii, 397.

ides and potassium hydroxide by the use of a form of the Debye equation for extrapolation to zero concentration.[13] The activities and activity coefficients of a number of salts in aqueous solution (and in some salt solutions) are thus known with considerable accuracy. The activity coefficients of a number of salts are plotted in Fig. 2 against their concentrations.

It will be observed that with increasing concentration the activity coefficient first diminishes, reaches a minimum, and rises again,

FIG. 2.



becoming greater than unity at high concentrations. This behaviour appears to be general.

The first attempt to obtain a general formula for the change of activity coefficient with concentration was made by G. N. Lewis and G. A. Linhart,[14] who showed that in very dilute solution the observed values could be represented by an equation of the type $\log f = -\beta c^{\alpha'}$, where β and α' are constants. G. N. Lewis and M. Randall[15] suggested the empirical rule that for uni-univalent electrolytes $\alpha' = 1/2$ and J. N. Brönsted[16] employed a similar

[13] G. Scatchard, *J. Amer. Chem. Soc.*, 1925, **47**, 648; *A.*, ii, 397.
[14] *Ibid.*, 1919, **41**, 1951; *A.*, 1920, ii, 97.
[15] "Thermodynamics," p. 345.
[16] *J. Amer. Chem. Soc.*, 1922, **44**, 938; *A.*, 1922, ii, 482.

relation, while B. A. M. Cavanagh [17] showed that an equation of this form followed from S. R. Milner's theory of electrolytes. Whilst such an equation covers the diminution of the activity coefficient at small concentrations, it is necessary to introduce another term to include the subsequent rise. Thus H. S. Harned [18] has given the empirical equation $\log f = -\beta c^{\alpha'} + \alpha c$, where α is a third constant, and has shown that values of the constants can be found which satisfactorily reproduce the observed values over a wide range of concentration. J. N. Brönsted employed the similar equation $\log f = -0{\cdot}42c^{1/2} + \alpha c$ for uni-univalent electrolytes.[19]

The activity coefficient of an electrolyte at fixed concentration in the presence of increasing concentrations of other salts follows a similar course, but the magnitude of the effect varies considerably according to the valence type of the salts. In order to eliminate differences of the electric forces in equal concentrations of ions of different valencies, Lewis and Randall [20] introduced a quantity called the ionic strength (μ), obtained by multiplying the concentration of each ion by the square of its valency and dividing the sum of the products by two. They were then able to state the general principle that in dilute solutions "the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength." In stronger solutions, deviations appear owing to the individual behaviour of ions.

Turning now to the attempts to explain the behaviour of strong electrolytes in terms of interionic electric forces, the Debye-Hückel theory [21] has been greatly extended.[22a] P. Debye has given a more direct derivation of his fundamental equation of the relation between activity coefficient and concentration.[22b] The first step

[17] *Phil. Mag.*, 1922, [vi], **44**, 226, 610.

[18] *J. Amer. Chem. Soc.*, 1920, **42**, 1808; 1922, **44**, 252; *A.*, 1920, ii, 664; 1922, ii, 255.

[19] *Loc. cit.*, ref. 16.

[20] *J. Amer. Chem. Soc.*, 1921, **43**, 1112; *A.*, 1921, ii, 427.

[21] *Ann. Report*, 1924, p. 25.

[22] Bibliography below :—

(*a*) P. Debye and E. Hückel, "On the Theory of Electrolytes." I. The freezing point lowering and related phenomena, *Physikal. Z.*, 1923, **24**, 185; *A.*, 1923, ii, 459. II. The limiting law of electrical conductivity, *ibid.*, 1923, **24**, 305; *A.*, 1923, ii, 724. (*b*) P. Debye, "The Osmotic Equation of State and Activity of Dilute Strong Electrolytes," *ibid.*, 1924, **25**, 97; *A.*, 1924, ii, 386. (*c*) O. Schärer, "The Theory of Solubility Influences in Strong Electrolytes," *ibid.*, 1924, **25**, 145; *A.*, 1924, ii, 455. (*d*) P. Gross and O. Halpern, "On the Dilution Law and Distribution of Strong Electrolytes," *ibid.*, 1924, **25**, 393; *A.*, 1925, ii, 117. (*e*) A. Frivold, "Contribution to Knowledge of So-called Anomalous Properties of Strong Electrolytes," *ibid.*, 1924, **25**, 465; *A.*, 1925, ii, 396. (*f*) P. Debye and J. McAulay, "The Electric Field of

is the calculation of the electrical potential of an ion in the solution due to all the other ions about it, which is effected by the combined use of Boltzmann's equation and Coulomb's law. To a first approximation (neglecting the dimensions of the ion itself) it has the value $\psi = -e_i^2\kappa/D$, where e_i is the charge on the ion, D the dielectric constant of the medium, and κ a quantity characteristic of the solution which is given by $\kappa^2 = \frac{4\pi}{DkT}\Sigma n_i e_i^2 = \frac{8\pi\varepsilon^2}{DkT}\frac{N}{1000}\mu$, in which n_i is the number of ions of the i^{th} kind per c.c. in the solution, ε the charge on a univalent ion, N the Avogadro number, k the gas constant per molecule, and μ the ionic strength. Instead of calculating the total electrical energy as before,[22a] Debye now deduces the work, W, which must be done in giving the ions their charge, assuming them to be initially uncharged; $W = \Sigma n_i e_i \psi_i/3$ for all the ions in one c.c.

The free energy of the system is greater by this amount than if there were no electric forces between the ions, *i.e.*, $\Sigma\Delta F = \Sigma N_i kT \log c_i/c_i^0 + W$; * actually $\Sigma\Delta F = \Sigma N_i kT \log f_i c_i/c_i^0$, whence it is only a matter of mathematics to deduce the result,

$$\log_e f_i = -\frac{\varepsilon^2 z_i^2 \kappa}{2DkT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

for a single ion,

and

$$\log_e f = -\frac{\varepsilon^2\kappa}{2DkT}\frac{\Sigma\nu_i z_i^2}{\Sigma\nu_i} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

for a salt giving ν_i ions of valency z_i. For an electrolyte giving ions of valencies $z_1 z_2$ this reduces to $\log_{10} f = z_1 z_2 B\sqrt{\mu}$ and at 0° $B = 0{\cdot}5$.

It must be clearly understood that these equations represent

* For brevity, summation is taken to include the solvent and all the kinds of ions present.

Ions and Neutral-salt Action," *ibid.*, 1925, **26**, 22; *A.*, ii, 171. (*g*) E. Hückel, "On the Theory of Concentrated Aqueous Solutions of Strong Electrolytes," *ibid.*, 1925, **26**, 93; *A.*, ii, 513. (*h*) O. Redlich, "On the Theory of Electrolytic Conductivity," *ibid.*, 1925, **26**, 199; *A.*, ii, 541. (*i*) P. Gross and O. Halpern, "On the Temperature-dependent Parameter in Statistics and the Debye Theory of Electrolytes, *ibid.*, 1925, **26**, 403; *A.*, ii, 866. (*j*) A. A. Noyes, "Interionic Attraction Theory of Ionised Solutes." I. "Critical Presentation of the Theory," *J. Amer. Chem. Soc.*, 1924, **46**, 1080; *A.*, 1924, ii, 658. II. "Testing the Theory with Experimental Data," *ibid.*, p. 1098; *A.*, 1924, ii, 659. (*k*) A. A. Noyes and W. P. Baxter, III. "Testing the Theory in Alcohol Solvents," *ibid.*, 1925, **47**, 2122; *A.*, ii, 970. (*l*) P. Debye and L. Pauling, IV. "The Influence of Variation of Dielectric Constant on the Limiting Law," *ibid.*, p. 2129; *A.*, ii, 970. (*m*) P. Gross and O. Halpern, "Electrolytes in Solutions of Low Dielectric Constant," *Physikal. Z.*, 1925, **26**, 636; *A.*, ii, 1152. (*n*) Compare also J. J. van Laar, "On the Theory of Strong Electrolytes and its History," *Z. anorg. Chem.*, 1924, **139**, 108.

the "limiting law" at very small concentrations; in most cases considerable deviations occur below 0·1*N*. A. A. Noyes [22j] discussed a large body of data and came to the conclusion that although deviations begin at quite small concentrations, the evidence supported the truth of the equation in limiting cases. J. N. Brönsted and V. K. LaMer [23] have since determined the activity coefficients of a number of complex cobaltammines of various valence types in dilute salt solutions up to 0·02*N*, and find that they are completely in accordance with the Debye equations. F. Hovorka and W. H. Rodebush [24] have determined the freezing points of solutions of seven electrolytes between 0·01 and 0·001*M*, "which show rather remarkable agreement with the values derived from the formula of Debye and Hückel."

On the other hand, M. Randall and A. P. Vanselow [25] find that the freezing points of solutions of hydrogen chloride, thallous chloride, and lead nitrate are not in good agreement. G. Scatchard,[26] however, claims that they are in agreement with the modified equation discussed below.

The first step in the extension of the theory to more concentrated solutions is to take account of the size of the ions. If the ion has finite size, the expression for the potential becomes

$$\psi_i = -\frac{z_i\varepsilon}{D}\frac{\kappa}{1+\kappa a_i},$$

where a_i is the mean least distance of approach of the centre of any ion to that of the ion in question. The activity coefficient equations become

$$\log_e f_i = -\frac{z_i^2\varepsilon^2}{2DkT}\frac{\kappa}{1+\kappa a_i} \quad . \quad . \quad . \quad . \quad (3)$$

and

$$\log_e f = -\frac{z^2 B\sqrt{\mu}}{1+Aa\sqrt{\mu}} \quad . \quad . \quad . \quad . \quad (4)$$

assuming that the mean ionic radius has a mean value, a, for all ions.

It has been shown by Scatchard [26] that this is equivalent to the empirical equation $\log f = -\beta c^{1/2} + \alpha c$, and $\beta = 0{\cdot}5$ for uni-univalent salts. O. Schärer has applied equation (4) to the solubilities of salts in salt solutions.[22c] The ionic radius term a is unknown and is an adjustable variable in the equation. He finds the values which reproduce the experimental data best by a graphical method, and thus obtains equations which completely represent the solubilities

[23] *J. Amer. Chem. Soc.*, 1924, **46**, 555; *A.*, 1924, ii, 306.
[24] *Ibid.*, 1925, **47**, 1614; *A.*, ii, 772.
[25] *Ibid.*, 1924, **46**, 2418; *A.*, 1925, ii, 33. [26] *Loc. cit.*, ref. 12.

of calcium sulphate, silver sulphate, thallous chloride, and various cobaltammine salts in salt solutions, with and without a common ion.

A. A. Noyes [27] pointed out that there is an irreconcilable difference between the results of the Debye and the Milner [28] calculations of the inter-ionic energy. The two theories have been further critically compared by S. R. Pike and G. Nonhebel,[29] who come to the conclusion that neither can do more than indicate the form of the equation. G. Nonhebel and H. Hartley [30] have examined the activity coefficients of hydrogen chloride in methyl alcohol, ethyl alcohol, and water with the same object. Whereas the Debye calculation leads to the expression $-\log f = \beta\sqrt{c} - \alpha c$, the Milner equation becomes $-\log f = 1{\cdot}018\beta f(c)\sqrt{c}$, where $f(c)$ is a tabulated function of the concentration. These authors conclude that the Milner equation without any adjustable constant α represents the data better than the Debye formula with one, and find that the activity coefficients are well represented by empirical equations of the form $-\log f = \beta'\sqrt{c}$ and that the values of β'/β are in good agreement with the Milner function $f(c)$ at $0{\cdot}0005n$. Further work on this discrepancy will be welcome.

R. H. Fowler [31] has examined the range of validity of the combined use of Boltzmann's and Poisson's equations with particular reference to the Debye-Hückel theory and concludes that the validity of this theory cannot be regarded as established except for small values of the ionic concentrations.

The Debye equation has been tested on another point (in which it agrees with the Milner equation). The fundamental equation indicates that at the same concentration in different solvents $\log f \propto 1/D^{3/2}$. This requirement has been confirmed by A. A. Noyes and W. P. Baxter,[32] using the data for lithium chloride, hydrogen chloride, and sodium ethoxide in ethyl alcohol, and by G. Nonhebel and H. Hartley.[33]

It will be observed that equations (1)—(4), in which $\log f$ is necessarily negative, cannot account for the rise of the activity coefficient above unity in concentrated solutions. In order to explain this, Hückel [22g] has considered the change of dielectric constant of the solution with concentration. It is assumed that the addition of

[27] *Loc. cit.*, ref. 22, *j*, *I*.

[28] *Phil. Mag.*, 1912, [vi], **23**, 551; 1913, **25**, 742; 1918, **35**, 214, 352; *A.*, 1913, ii, 481; 1918, ii, 54, 148; *Trans. Faraday Soc.*, 1919, **15**, 148; *A.*, 1920, ii, 152.

[29] *Phil. Mag.*, 1925, [vi], **50**, 723; *A.*, ii, 1061.

[30] *Loc. cit.*, ref. 8.

[31] *Proc. Camb. Phil. Soc.*, 1925, **22**, 861.

[32] *Loc. cit.*, ref. 22, *k*.

[33] *Loc. cit.*, ref. 8. Compare also G. Scatchard, *J. Amer. Chem. Soc.*, 1925, **47**, 2098; *A.*, ii, 971.

salts causes a lowering of the *D.C.* by an amount proportional to the concentration, as expressed by the formula $D = D_0 - \Sigma\delta c$, where δ is the lowering produced by unit concentration of one particular kind of ion. A change of *D.C.* involves, in addition to its effect on the Coulomb law expression, a change in the electrical energy of the ions themselves in the medium. If it be supposed that the charge e_i is located on a sphere of radius b_i, the potential at the surface is e_i/Db_i and the corresponding electrical energy $e_i^2/2Db_i$. In bringing the ions from an infinitely dilute solution ($D.C. = D_0$) to a solution of $D.C. = D$, the electrical energy will increase by

$$\omega = -\Sigma N_i \frac{e_i^2}{2D_0 b_i} + \Sigma N_i \frac{e_i^2}{2Db_i}$$

and this term must be added to the Coulomb expression in order to obtain the complete electrical work term. In order to simplify the calculation, Hückel puts $a_i = b_i$ and uses a mean value, a, for all the ions present, thus obtaining the result:

$$\log f_i = -\frac{z_i^2\varepsilon^2}{2D_0 kT}\frac{\kappa_0}{1+\kappa_0 a} + f(\kappa) \quad . \quad . \quad . \quad (5)$$

where $f(\kappa)$ is a complicated function of κ which is found on calculation to be nearly proportional to the concentration. Hence for a uni-univalent salt

$$\log f = -\frac{B\sqrt{c}}{1+Aa\sqrt{c}} + C \,.\, 2c \quad . \quad . \quad . \quad (6)$$

where A and B have the same values as before and C is a third constant. Values of C corresponding to various values of δ are calculated and that value which fits the observed data best is selected. The activity coefficients of lithium, sodium, and potassium chlorides over the whole range of concentration are given by the equation, assuming the values of the *D.C.* lowering coefficient, δ, to be 20, 9, and 6, respectively. Equally good agreement with the observed results for hydrogen chloride was obtained both on the assumption that the hydrogen ion is free (H^+) and that it exists as the hydrate (H_3O^+), different values of the constants being required for the two cases.

It would appear that a considerable step forward in our knowledge of the factors determining the behaviour of salt solutions has been made. It must be remembered, however, that in the final equation there are two variable factors which can be selected to fit the observed results. The outcome is not, therefore, a calculation of activities from fundamental data, and until the constants have been obtained independently the theory must be regarded as a

derivation of the form of the empirical equation, taking account of inter-ionic forces and the dielectric constant.

The somewhat artificial character of the calculation is realised by Debye and Hückel, and the latter has given an exhaustive discussion of the factors concerned in concentrated aqueous solutions.[34] The high dielectric constant of water means high polarisability in an electric field and the presence of molecules which act as electric "dipoles." In the intense electric fields in the vicinity of ions the dipoles must be oriented and owing to the intensity of the forces [35] it is probable that "electric saturation," *i.e.*, total possible orientation, occurs. Each ion is therefore surrounded by an atmosphere of water "bound" by electrostatic forces. An applied electric field must have a smaller effect on solvent molecules in the vicinity of ions than on the unoriented solvent, hence the dielectric constant is lowered by the presence of ions. This view was originally put forward by K. Fajans,[36] and M. Born [37] has shown that the hydration energy of ions can be accounted for on the same basis.

The salting-out effect of non-electrolytes by salts has been discussed by P. Debye and J. McAulay [22f] from the same point of view. The effect of introducing a strong electrolyte into a solution of a non-electrolyte, according to these authors, is to cause the more polarisable components to amass themselves round the ions, where the electric field is great. If the solvent has the greater polarisation capacity, the effect is a displacement of the non-electrolyte from the vicinity of the ion (*i.e.*, an apparent diminution of the solution volume) and a rise in its activity. If the non-electrolyte is more polarisable than the solvent and raises its *D.C.*, the effect is the reverse. Calculations of the increase of the activity of non-electrolytes by salts on these lines agree with the magnitude of the effect.[38] The importance of these theories on the question of hydration in solution is obvious, but it is felt that the time is scarcely ripe for a general discussion.

P. Gross and O. Halpern have further considered [22m] the behaviour of electrolytes in solvents of low dielectric constant. They find that the effect of the ionic charges on the osmotic properties may be not only small, but also in the reverse direction of the Coulomb effect described above. The solute will thus appear to be associ-

[34] *Loc. cit.*, ref. 22, *g*.

[35] At 3×10^{-8} cm., Hückel estimates the potential gradient at 2×10^{6} volts per cm.

[36] *Ber. Deut. Physikal. Ges.*, 1919, **21**, 549, 709; *A.*, 1920, ii, 12, 154.

[37] *Z. Physik*, 1920, **1**, 45; *A.*, 1921, ii, 166. Compare also O. Blüh, *ibid.*, 1924, **25**, 220; *A.*, 1924, ii, 824; *Naturwiss.*, 1921, p. 732.

[38] Compare also E. A. Hafner and L. von Kürthy, *Arch. exp. Path. Pharm.*, 1924, **104**, 148; *A.*, 1925, ii, 283.

ated. They are able to account qualitatively for the various types of anomalous behaviour observed in non-aqueous solutions.

The determination of the dielectric constants of solutions of electrolytes has thus become a matter of considerable importance. Until recently no direct means of measurement was available, but the difficulty has been overcome by the use of electric oscillations of short wave-length.[39] The lowering of the *D.C.* of water by salts is confirmed. In the case of electrolytes such as tetrapropylammonium iodide in alcoholic solvents, the initial decrease is followed by a rise.

Conductivity of Strong Electrolytes.

On the theory of complete dissociation the change of the equivalent conductivity of a strong electrolyte with dilution is ascribed to changes in the inter-ionic forces. The theory of J. C. Ghosh did not survive criticism.[40] P. Debye and E. Hückel[41] have treated the conductivity problem on the same basis as their theory of osmotic properties. It was there postulated that every ion is immediately surrounded by an excess of ions of opposite charge. When the ion is in motion through the solution, a finite time is required for the redistribution of ions in this fashion (period of relaxation) and there will always be an excess of ions of opposite sign in its rear, hence it will be subject to a retarding force. Further, since ions of opposite sign are moving in different directions and drag with them a certain amount of solvent, the viscous resistance to the motion of an ion will be greater than if the other ions were at rest. Assuming Stokes's law, Debye and Hückel have computed these effects and deduced the relation for dilute solutions:

$$\Lambda_0 - \Lambda_c = \Lambda_0(K_1 w_1 + K_2 b)\sqrt{2c},$$

where Λ_0 and Λ_c are the equivalent conductivities at infinite dilution and at concentration c, $w_1 = 1/2\{l_a/l_c + l_c/l_a\}$, l_a and l_c being the mobilities of anion and kation, b the mean ionic radius, K_1 and K_2 constants depending on the temperature and *D.C.* of the medium. The first term in the bracket represents the period of relaxation effect, the second the viscosity effect. This equation agrees with the empirical relation found by Kohlrausch[42] for the conductivity of dilute salt solutions, $\Delta_0 - \Lambda_c = x\sqrt{c}$. Using a modified form of

[39] R. T. Lattey, *Phil. Mag.*, 1921, [vi], **41**, 829; *A.*, 1921, ii, 426; K. Theodortschick, *Physikal. Z.*, 1922, **23**, 344; P. Walden, H. Ulich, and O. Werner, *Z. physikal. Chem.*, 1924, **110**, 43; 1925, **115**, 117; 1925, **116**, 261; *A.*, ii, 512, 773.

[40] *Ann. Report*, 1918, 11; 1919, 14.

[41] *Loc. cit.*, ref. 22, *a*, II.

[42] *Z. Elektrochem.*, 1907, **13**, 333; *A.*, 1907, ii, 600.

Stokes's law, O. Redlich [43] has obtained a modified equation which gives exact agreement with the experimental results for aqueous solutions. J. E. Frazer and H. Hartley [44] have determined the conductivities of fifteen univalent salts in methyl alcohol and find that although they agree with the form of the equation, they are not consistent with the value of w given above, indicating that some revision of the theory is necessary in this respect. C. W. Davies [45] also has given an empirical equation which is in good agreement with the data of aqueous solutions, viz.: $\Lambda_0 - \Lambda_c = K\sqrt{c}(\sqrt{l_c} + \sqrt{l_a})$. According to Frazer and Hartley, this is not applicable to methyl-alcoholic solutions. A. Ferguson and I. Vogel [46] have used an empirical equation of the form: $\Lambda_0 - \Lambda_c = Bc^n$.

Activities in Binary Liquid Mixtures and Deviations from Raoult's Law.

Activities in binary liquid mixtures of non-electrolytes have also received much attention in recent years. The most general expression of Raoult's law of perfect solutions is that the activity of a component (taken as unity for the pure liquid) is equal to the mol.-fraction. The deviations from Raoult's law which occur in many systems have been widely discussed in the past and have been attributed exclusively to chemical and to physical effects. The attempt to explain all deviations chemically (*e.g.*, by solvation and association) failed, although they certainly occur in some systems. Attention has therefore been focussed on purely physical effects. A comprehensive theory of liquid mixtures has been developed by J. H. Hildebrand and collaborators.[47] In a perfect solution a molecule of any component behaves exactly as if in its own pure liquid, and any deviation from ideality must be due to the difference between the forces acting on a given molecule in the solution and when it is surrounded solely by molecules of its own kind (*i.e.*, in the pure liquid component). Deviations will obviously be least with liquids of very similar nature in which the intermolecular forces are nearly identical. As a measure of the forces between molecules in different liquids Hildebrand has taken the internal pressure. He has obtained concordant values of this quantity from a variety of properties, the constants of van der Waals's equation, surface

[43] *Loc. cit.*, ref. 22, *h*.

[44] *Proc. Roy. Soc.*, 1925, *A*, **109**, 351; *A.*, ii, 1163.

[45] *J. Physical Chem.*, 1925, **29**, 473, 973, 977; *A.*, ii, 541, 871.

[46] *Phil. Mag.*, 1925, [vi], **50**, 971; *A.*, ii, 1163.

[47] *J. Amer. Chem. Soc.*, 1916, **38**, 1452; 1917, **39**, 2297; 1919, **41**, 1067; 1920, **42**, 2180, 2213; 1921, **43**, 500, 2172; 1923, **45**, 682, 2828; *A.*, 1916, ii, 518; 1918, ii, 36, 65; 1919, ii, 392; 1921, ii, 23, 24, 307; 1922, ii, 141; 1923, ii, 315; 1924, ii, 94; J. H. Hildebrand, "Solubility" (Chem. Cat. Coy)., 1924.

tension, heat of vaporisation, and from solubility data, and has shown that deviations from Raoult's law are qualitatively proportional to the internal pressure difference of the components.

This theory has been extended to solubility relations by the consideration of the solubility curve up to the melting point of the solute, at which the solubility expressed as mol.-fraction in the liquid phase is unity. The "ideal" solubility curve for solutions which obey Raoult's law is given by the relation : $d \log N/d(1/T) = -L_f/4{\cdot}58$, where N is the mol.-fraction of solute, and L_f the latent heat of fusion of solute. Hence, if $\log N$ is plotted against $1/T$, a straight line is obtained for an ideal solution having the slope $-L_f/4{\cdot}58$. When the solubility curves of a given solute in a number of solvents are plotted in this way a family of curves is obtained deviating more or less from the ideal line. Such sets of curves have been obtained for naphthalene,[48] iodine,[48] sulphur,[49] and a number of organic compounds.[50] The ratio of the actual slope of the solubility curve to the ideal slope (a factor f) has been shown by F. S. Mortimer [50] to be related to the internal pressures of the solvent and solute by the equation $f = K_1 - K_2 + 1$, where K_1 and K_2 are the relative internal pressures, referred to naphthalene as unity. He has described a chart by which the proper factor can be read off for any pair of substances the relative internal pressures of which are known. It is thus possible to predict the mutual solubilities of many non-polar or slightly polar substances with some precision.

Whilst Hildebrand's theory gives a qualitative indication of deviations from Raoult's law over a wide field, it has not been developed quantitatively. J. A. V. Butler [51] considers that the partial heat of solution is a better measure of the difference between the forces acting on the molecules of a component in solution and in their pure liquids, and shows that in the case of thallium amalgams,[52] the logarithm of the activity coefficient, which represents the deviation from Raoult's law, is almost exactly proportional to the partial heat of solution. Close proportionality is also shown by the less accurate data of a number of binary alloys.[53]

[48] J. H. Hildebrand and C. A. Jenks, *J. Amer. Chem. Soc.*, 1920, **42**, 2180; *A.*, 1921, ii, 23.

[49] *Idem*, *ibid.*, 1921, **43**, 2172; *A.*, 1922, ii, 141.

[50] F. S. Mortimer, *ibid.*, 1922, **44**, 1416; 1923, **45**, 633; *A.*, 1922, ii, 621; 1923, ii, 299.

[51] *Ibid.*, 1925, **47**, 117; *A.*, ii, 539.

[52] T. W. Richards and F. Daniels, *ibid.*, 1919, **41**, 1732; G. N. Lewis and M. Randall, *ibid.*, 1921, **43**, 233; *A.*, 1920, ii, 34; 1921, ii, 241.

[53] N. W. Taylor, *ibid.*, 1923, **45**, 2865; *A.*, 1924, ii, 89.

The Galvanic Cell and Potential Differences.

The seat of the electromotive force in the galvanic cell has been discussed afresh by J. A. V. Butler.[54] The establishment of the Gibbs-Helmholtz relation between the electrical energy produced and the total energy of the reaction going on in the cell, and the wide use of the Nernst relation between the electrode potential and concentration of metal ions caused attention to be focussed almost exclusively on the chemical effects at the electrodes as the principal sources of the electromotive force. Recent physical investigations [55] on the thermionic and photoelectric properties of metals have, however, demonstrated conclusively the existence of large metal contact *P.D.*'s. The question arises, How are these to be reconciled with the "chemical" theory and in particular with the correspondence between the electromotive force and the energy of the chemical reaction? Butler meets this by showing that the energy of transfer of electrons from one metal to another, on which the metal contact *P.D.* depends, is an integral part of the energy of the chemical reaction. Thus the reaction $Zn + Cu^{\cdot\cdot} = Cu + Zn^{\cdot\cdot}$ which occurs in the Daniell cell consists of three parts: (1) the passage of zinc ions from the metal into the solution, (2) the deposition of copper ions on the copper, and (3) the transfer of electrons from the metallic zinc to copper. It is shown that the energy change of the third part is large, in fact of the same order of magnitude as the total energy of the reaction. In the galvanic cell the three stages occur at the two electrodes and at the metal junction, and each gives rise to its appropriate *P.D.* It thus appears that the two conflicting theories of the galvanic cell, the "chemical" and the "physical," are finally reconciled.

It is further pointed out that the existence of large metal contact *P.D.*'s has an important bearing on the determination of the absolute electrode potentials. The possibility of a metal junction *P.D.* between the metal investigated and the reference electrode has been overlooked, and it is likely that the discordant results obtained in methods employing mercury and those using other metals is due to this cause.

J. A. V. Butler has further given a kinetic theory of the *P.D.* at metal electrodes (Nernst *P.D.*),[56] at oxidation electrodes,[57] and at

[54] *Phil. Mag.*, 1924, [vi], **48**, 927; *A.*, 1925, ii, 42.

[55] O. W. Richardson and K. T. Compton, *ibid.*, 1912, [vi], **24**, 592; *A.*, 1912, ii, 1039; R. A. Millikan, *Physical Rev.*, 1916, **7**, 18; 1921, **18**, 236; A. E. Hennings and W. H. Kadesch, *ibid.*, 1916, **8**, 209.

[56] *Trans. Faraday Soc.*, 1924, **19**, 729; *A.*, 1924, ii, 598; compare *Ann. Report*, 1924, p. 17.

[57] *Trans. Faraday Soc.*, 1924, **19**, 734; *A.*, 1924, ii, 598.

metal junctions.[58] The expression obtained for the electrode potential of a metal is :

$$\mathrm{E} = \frac{U}{nF} + \frac{RT}{nF} \log K + \frac{RT}{nF} \log c,$$

in which U is the total energy change of the transfer of metal ions from the metal to the solution and K is a small constant characteristic of the metal. The first two terms are equivalent to the Nernst "solution pressure." By means of a cyclic process,[59] it has been shown that

$$U = S + J - H - \phi F,$$

where S is the latent heat of vaporisation of the metal, J is the energy required to ionise it in the vapour state, H is the hydration energy of metal ions, and $-\phi F$ the heat evolved in returning the electrons to the metal (ϕ = thermionic work function).

J. Heyrovský [60] also has discussed the factors determining the Nernst potential and by means of a thermodynamical argument has obtained a somewhat similar expression :

$$\pi_{\mathrm{Me}} = -\frac{RT}{F} \log P - \frac{H}{F} + \frac{RT}{F} \log c,$$

in which P includes quantities which depend on the metal alone and is regarded as the real "solution pressure." However, it may be noted that the electrode potentials calculated by this expression differ from the observed much more widely than those obtained by assuming that the electrical energy is simply equivalent to the total energy of the cell, and it is concluded from a similar argument that the metal contact *P.D.* is small (not greater than 0·2 volt), which is contrary to a large body of experimental evidence.

J. Heyrovský [61] and collaborators have published an extensive series of researches on electrolysis with the dropping mercury cathode. An instrument called the polarograph is described [62] which automatically records decomposition curves. It is claimed that the dropping mercury cathode has a number of advantages over electrodes hitherto employed. A fresh surface is continually exposed, reversible polarisation curves are obtained with very minute currents and the hydrogen overvoltage is the highest which has been observed. A variety of problems has been investigated

[58] *Phil. Mag.*, 1924, [vi], **48**, 746.

[59] *Loc. cit.*, ref. 54.

[60] *J. Physical Chem.*, 1925, **29**, 344, 406; *A.*, ii, 404, 544; *Rec. trav. chim.*, 1925, **46**, 447; *A.*, ii, 672; *Compt. rend.*, 1925, **180**, 1655; *A.*, ii, 793.

[61] *Trans. Faraday Soc.*, 1924, **19**, 692; *A.*, 1924, ii, 598; *Rec. trav. chim.*, 1925, **44**, 488–606; *A.*, ii, 673–678.

[62] J. Heyrovský and M. Shikata, *ibid.*, p. 496.

by its use. Its value has been strikingly shown by its independent indication of dvi-manganese in manganese salts.[63]

Two important papers on the Donnan membrane equilibrium have appeared. The data of F. G. Donnan and A. J. Allmand [64] on the distribution of potassium chloride between a pure aqueous solution and a solution containing potassium ferrocyanide, separated by a membrane impermeable to the ferrocyanide ion, have been recalculated in terms of activities instead of concentrations by N. Kameyama.[65] The distribution equilibrium found is in accordance with the ionic strength principle. R. Azuma and N. Kameyama [66] have investigated the potential difference and equilibrium of sodium chloride and Congo-red across a semipermeable collodion membrane. Assuming that Congo-red ionises as a uni-univalent electrolyte and the ionic strength principle holds, the equilibrium results are in agreement with the theory. It was not possible to prove that the *P.D.* was in agreement with the theoretical value, owing to the difficulty of eliminating liquid–liquid potentials. The theory of membrane equilibria has been restated by E. Hückel,[67] in relation to the Debye-Hückel theory.

In conclusion, the Reporter desires to thank Mr. J. A. V. Butler for the great help he has given in the preparation of this Report.

J. E. Coates.

[63] V. Dolejšek and J. Heyrovský, *Nature*, 1925, **116**, 782; A. N. Campbell, *ibid.*, p. 866; J. Heyrovský, *ibid.*, 1926, **117**, 16.

[64] *J.*, 1914, **105**, 1941.

[65] *Phil. Mag.*, 1925, [vi], **50**, 849; *A.*, ii, 1062.

[66] *Ibid.*, p. 1264.

[67] *Kolloid-Z.* (Zsigmondy Festschrift), 1925, **36**, 204; *A.*, ii, 528.

INORGANIC CHEMISTRY.

In the preparation of the Report for 1925 the task of selection has proved as difficult as ever, and it is necessary again to draw attention to the fact that many researches of interest and importance are omitted, or dismissed with a mere mention, often because their significance can only be appreciated on careful study, whereas this Report is written primarily for those who lack time for such study.

Perhaps the most marked general tendency is seen in the increasing application of physical methods and criteria to chemical problems, whereby it happens that much matter that could properly be included in this Report belongs as much to the preceding Report and may there be found. Those of us who have always regretted the artificial, although apparently convenient, line drawn between chemistry and physics welcome the incursions of physicists into chemistry and of chemists into physics which now so frequently occur.

Subjects which appear to the Reporter to be of rather special interest are: the formation of compounds of helium; the long-delayed confirmation of the production of helium in discharge tubes described by Collie and Patterson; the reported production of gold by electrical discharges in mercury vapour; the production of a new peroxide of barium; the evidence that the atomic weight of boron may vary with its source; the proof that carbon can be melted and the determination of its melting and boiling points; the isolation of pure tin hydride, a new oxide and persulphide of nitrogen, nitronium perchlorates, bromoazoimide, and the pseudo-halogen radicals oxycyanogen and selenocyanogen; the proof of the existence of sulphur sesquioxide; and the detection of two hitherto unknown elements of the manganese group. These matters, and many others which chemists may find of equal or greater interest, are dealt with, all too briefly, in their appropriate order.

Atomic Weights.

Hydrogen, Lithium, Carbon.—Using a new modification of the mass-spectrograph and the bracketing method of observation, with helium = 4·000 as standard, the values H = 1·0079 and C = 12·000 have been found. By the same method, it has been found that if N = 14·008, the lithium isotopes have the atomic weights Li^6 = 6·009 and Li^7 = 7·012.[1]

[1] J. L. Costa, *Compt. rend.*, 1925, **180**, 1661; *Ann. Physique*, 1925, [x], **4**, 25; *A.*, ii, 619, 1021.

Boron.—Determinations of the ratio $BCl_3 : 3Ag$ by nephelometric titration with weighed silver in the usual manner, using boron trichloride prepared from boron minerals of known and widely separated origin, have given evidence of a variation in the atomic weight of boron. Boron from California gave B = 10·840, whilst samples from Tuscany and Asia Minor gave B = 10·825 and B = 10·818, respectively: these results indicate that the Californian boron contains about 2% more of the isotope B^{11} than do the other samples.[2] Should the observation be confirmed, we have here the first known case of a natural variation in the atomic weight of one of the lighter elements and it will become of interest to inquire whether this variation existed originally or has resulted from a partial separation of isotopes occurring in nature through the peculiar mode of formation of boron minerals by volatilisation of boron compounds.

The mean result now obtained is in agreement with those previously reported,[3] but differs considerably from the mean of earlier data, which were largely based on analyses of borax: it is therefore of interest that a critical examination of the titration of borax glass with hydrochloric acid standardised against silver has shown that borax loses soda on fusion, that the glass is indefinite in composition, and that values of the atomic weight based on the use of this material are untrustworthy.[4]

Carbon, Nitrogen.—An extension of earlier work on the densities and compressibilities of ethylene, nitrous oxide, and nitric oxide has given the values: C = 12·000 and N = 14·003; N = 14·006.[5]

Aluminium.—Using pure aluminium chloride prepared by the action of chlorine on alumina and carbon at a red heat, five determinations of the ratio $AlCl_3 : 3Ag$ and two of the ratio $AlCl_3 : 3AgCl$ gave in mean Al = 26·971.[6]

Silicon.—Silicon tetrachloride, purified by repeated distillation in a high vacuum until it gave a constant vapour pressure, was decomposed by sodium hydroxide solution and used to determine the ratio $SiCl_4 : 4Ag$.

Four analyses gave in mean Si = 28·105 ± 0·003 (mean deviation), confirming Baxter's value (28·063) as against that (28·3) formerly accepted.[7] An attempt has been made to test the con-

[2] H. V. A. Briscoe and P. L. Robinson, *J.*, 1925, **127**, 696.

[3] *Ann. Reports*, 1922, **19**, 34.

[4] H. V. A. Briscoe, P. L. Robinson, and G. E. Stephenson, *J.*, 1925, **127**, 150.

[5] T. Batuecas, *J. Chim. phys.*, 1925, **22**, 101; *A.*, ii, 497.

[6] H. Křepelka and N. Nikolić, *Chem. Listy*, 1925, **19**, 158; *A.*, ii, 620.

[7] O. Hönigschmid and M. Steinheil, *Z. anorg. Chem.*, 1924, **141**, 101; *A.*, 1925, ii, 174.

stancy of the atomic weight of silicon from various sources, terrestrial and meteoritic: comparison of the densities of carefully purified samples of tetraethylsilicane prepared from these sources disclosed no difference greater than that corresponding to a variation of about 0·02 in the atomic weight: the fact that the variations in refractive index of the samples showed a general parallelism with the variations in density was held to indicate that the observed density variations were, at least in part, due to varying proportions of impurities and hence that the real variation in the atomic weight of silicon is less than 0·02.[8]

Chlorine.—Redeterminations of the density and compressibility of methyl chloride yield for chlorine the value Cl = 35·47.[9] Approximate evidence has been obtained for the constancy of the isotope ratio for chlorine, as no difference could be detected in the proportions of chlorine present in silver chloride prepared (*a*) from volcanic ammonium chloride from Vesuvius, (*b*) from water at a depth of 1573 m. in the Calumet and Hecla mines near Lake Superior, and (*c*) from ordinary barium chloride;[10] and the atomic weight of chlorine from "shale balls" associated with the Canyon Diabolo meteorite (although this chlorine is doubtfully of meteoritic origin) was found not to differ from that of "ordinary" chlorine by more than 1 part in 2000 parts.[11]

Copper.—The rejection by the German Commission on Atomic Weights of the value reported last year[12] has led to a series of experiments which shows that homogeneous cupric oxide, free from occluded gases, is in fact obtained by heating the oxide first at 1000° in air and then in oxygen and finally for a long period at about 700° in oxygen. Hence the value Cu = 63·546 is reaffirmed.[13]

Selenium.—Hydrogen selenide was prepared from carefully purified selenium, either by direct union with hydrogen at 700° or by the action of water on aluminium selenide, and purified by condensation at − 80°. As a mean of 53 determinations by direct weighing, the normal litre of hydrogen selenide weighs 3·6624 grams, whence the atomic weight of selenium is Se = 79·23.[14]

Bromine.—Ammonium bromide was subjected to a prolonged systematic fractional crystallisation involving about 2700 crystal-

[8] F. M. Jaeger and D. W. Dijkstra, *Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 393; *A.*, 1925, ii, 83.

[9] T. Batuecas, *Compt. rend.*, 1925, **180**, 1929; **181**, 40; *A.*, ii, 753.

[10] (Mlle.) E. Gleditsch, *J. Chim. phys.*, 1924, **21**, 456; *A.*, 1925, ii, 174.

[11] A. W. C. Menzies, *Nature*, 1925, **116**, 643; *A.*, ii, 1109.

[12] *Ann. Reports*, 1924, **21**, 28.

[13] R. Ruer and K. Bode, *Ber.*, 1925, **58**, [*B*], 852; *A.*, ii, 620.

[14] P. Bruylants, F. Lafortune, and L. Verbruggen, *Bull. Soc. chim. Belg.*, 1924, **33**, 587; *A.*, 1925, ii, 174.

lisations and the bromine in the final head and tail fractions was rigorously purified by chemical means, re-converted into ammonium bromide, and used for gravimetric determinations of the ratio Ag : AgBr, employing a special apparatus and technique obviating transference of the silver bromide during the operations of precipitation, filtration, and weighing. Identical values were obtained for both end fractions, showing that fractionation had produced no change as great as 1% in the isotope-ratio, and the general mean value Br = 79·914 ± 0·003 differs by less than 1 part in 50,000 parts from Baxter's previous value, and confirms the accepted figure.[15]

Zirconium.—Samples of zirconium material used for atomic weight determinations by Venable and Bell[16] have been found to contain from 0·7% to 1·0% of hafnium : a correction being applied for this impurity, the atomic weight of zirconium is Zr = 91·3 ± 0·1.[17] This figure is confirmed by determinations of the bromide : silver ratio, similarly corrected for traces of hafnium present, yielding the value Zr = 91·22.[18]

Holmium.—Material purified by fractionation as bromate and by partial decomposition of the nitrate and shown to be free from yttrium and dysprosium by measurements of magnetic susceptibility was used for determinations of the ratio $HoCl_3$: 3Ag, giving the value Ho = 163·47.[19]

Hafnium.—Specimens of hafnium bromide of relatively high purity, in one case containing only 0·16% of zirconia, were prepared by igniting hafnia with sugar charcoal in a current of nitrogen saturated with bromine and analysed in the usual manner. The results, corrected for the effect of the small proportion of zirconium present, give for the atomic weight of hafnium, Hf = 178·6 ± 0·08.[20]

Lead.—Determinations of the ratio of lead chloride to silver, with samples of lead extracted from pitchblende from the Belgian Congo, have given the values Pb = 206·19 and 206·14.[21] Comparison of the atomic weight of lead from Norwegian cleveite with

[15] P. L. Robinson and H. V. A. Briscoe, *J.*, 1925, **127**, 138; compare Baxter, *J. Amer. Chem. Soc.*, 1906, **28**, 1322.

[16] F. P. Venable and J. M. Bell, *J. Amer. Chem. Soc.*, 1917, **39**, 1598; *A.*, 1917, ii, 479.

[17] G. Hevesy, *Nature*, 1925, **115**, 335; *A.*, ii, 255.

[18] O. Hönigschmid, E. Zintl, and F. González, *Anal. Fis. Quím.*, 1924, **22**, 432; *A.*, 1925, ii, 174.

[19] F. H. Driggs and B. S. Hopkins, *J. Amer. Chem. Soc.*, 1925, **47**, 363; *A.*, ii, 463.

[20] O. Hönigschmid and E. Zintl, *Ber.*, 1925, **58**, [*B*], 453; see also *Z. anorg. Chem.*, 1924, **140**, 335; *A.*, 1925, ii, 347, 255.

[21] H. Brennen, *Compt. rend.*, 1925, **180**, 282; *Ann. Chim.*, 1925, [x], **4**, 127; *A.*, ii, 174, 1109.

that of ordinary lead (207·18) by determining the ratio $PbCl_2 : PbSO_4$ and by measuring the densities of saturated solutions of the nitrates, has given for the former material the value Pb = 206·17.[22]

Bismuth.—In a repetition, with improved technique, of a method previously reported,[23] bismuth triphenyl purified by distillation in a vacuum was treated with oxalic acid and the resulting oxalate was ignited to oxide in an apparatus such that these operations involved no transference of material. Fifteen experiments gave in mean the value Bi = 208·989,[24] confirming the former determinations by the same method and in good agreement with the evidence afforded by the mass-spectrograph that bismuth is a simple element of mass number 209.[25]

Group O.

Under certain conditions, in the presence of an electric glow discharge, mercury and helium combine to form mercury helide. This substance, the simplest formula for which is $HgHe_{10}$, is a comparatively stable substance, but slightly absorbed in charcoal cooled with liquid air and decomposed at a bright red heat.[26] When helium is subjected to intense electronic bombardment at low pressures in contact with a heated tungsten filament, both elements disappear with formation of a black deposit which is decomposed by nitric acid or aqueous potassium hydroxide with evolution of helium to yield tungstic oxide or a clear solution. In the absence of mercury vapour, the atomic ratio of the loss in weight of the filament and the loss of helium was 1 : 2 and there is thus strong evidence for the formation of a stable compound WHe_2. From mixtures with the vapours of mercury, iodine, sulphur, and phosphorus subject to electronic bombardment in the vicinity of surfaces cooled with liquid air, helium disappears comparatively quickly and solid substances are obtained the behaviour of which suggests that they are compounds of helium stable at − 180° but decomposing at higher temperatures.[27] When helium was ionised by radon in presence of mercury, no evidence of compound formation could be obtained; but this is not necessarily at

[22] (Mlle.) E. Gleditsch, (Mme.) Dorenfeldt, and O. W. Berg, *J. Chim. Phys.*, 1925, **22**, 253; *A.*, ii, 732.

[23] *Ann. Reports*, 1921, **18**, 36.

[24] A. Classen and G. Strauch, *Z. anorg. Chem.*, 1924, **141**, 82; *A.*, 1925, ii, 175.

[25] F. W. Aston, *Phil. Mag.*, 1925, [vi], **49**, 1191; *A.*, ii, 618.

[26] J. J. Manley, *Nature*, 1924, **114**, 861; 1925, **115**, 337, 947; *A.*, ii, 57, 314, 696.

[27] E. H. Boomer, *Proc. Roy. Soc.*, 1925, *A*, **109**, 198; *Nature*, 1925, **115**, 16; *A.*, ii, 925, 144.

variance with the foregoing observations.[28] These are of special interest in that they may account for numerous failures to repeat the experiments of Collie and Patterson [29] indicating the production of helium and neon in discharge tubes. It has now been found that bombardment of the nitrides of magnesium and aluminium at the focus of a concave cathode in a tube containing oxygen produces helium, hydrogen, and neon, that discharge tubes after 60 hours' use, when powdered and heated at 800° in a vacuum, yield considerable amounts of helium, and that the rare gases were always obtained in discharge tubes when using an induction coil giving a 6-inch spark, but not with a larger coil.[30]

By compressing xenon in presence of water below 24°, the critical temperature of decomposition, a crystalline hydrate with 6 or 7 molecules of water is formed, the dissociation pressures of which have been measured over the range to 1·4°. Xenon hydrate, with a dissociation pressure of 1·15 atm. at 0°, is much the most stable of the hydrates of the inert gases.[31]

Group I.

The work of Coehn and Tramm [32] indicated that a mixture of oxygen and hydrogen dried sufficiently to preclude explosion on heating would, under the action of ultra-violet light, combine as readily as the undried gases. This work has been very carefully repeated using six pairs of quartz tubes filled over mercury with a gas mixture produced by electrolysis of an aqueous solution of very pure baryta, one tube of each pair containing pure phosphoric oxide. After drying in the dark for from 2 to 8 weeks, both tubes of each pair were exposed to the same radiation from a quartz mercury-vapour lamp for several hours and the extent of reaction, as measured by the rise of mercury in the tubes, was noted. In every case there was markedly less reaction in the dried tube than in the other, and in those dried for 7 or 8 weeks no measurable contraction occurred in 5 or 6 hours' exposure to radiation. No ozone was produced in either the wet or the dry gas.[33]

If an electric light bulb is partly immersed in molten sodium nitrate, and the filament is heated while a potential difference is maintained between it and a positive electrode in the fused salt, thermionic emission will allow a current up to 0·3 amp. to pass

[28] S. C. Lind and D. C. Bardwell, *Science*, 1925, **61**, 344; *A.*, ii, 1181.
[29] *J.*, 1913, **103**, 419.
[30] R. W. Riding and E. C. C. Baly, *Proc. Roy. Soc.*, 1925, *A*, **109**, 186; *A.*, ii, 925.
[31] De Forcrand, *Compt. rend.*, 1925, **181**, 15; *A.*, ii, 812.
[32] Coehn and Tramm, *Ber.*, 1922, **56**, 455.
[33] H. B. Baker and (Miss) M. Carlton, *J.*, 1925, **127**, 1990.

through the glass, and metallic sodium, in amounts up to 0·3 gram per hour, is deposited in the bulb. It is stated that sodium lamps, giving a pure sodium spectrum, may thus be prepared.[34]

Recrystallisation from anhydrous ammonia can yield sodium and potassium cyanides containing less than 0·1% of impurity and, by means of a gold–silver thermocouple, pure salts so prepared were found to have the m. p. 563·7° ± 0·3° and 634·5° ± 1°, respectively.[35]

An important report has been issued upon the corrosion of copper, brass, and zinc in sea-water.[36] Corrosion of copper, whether pure or in brass, occurs by primary formation of cuprous chloride, which, in presence of oxygen, is further oxidised to the basic chloride $Cu_4(OH)_6Cl_2,H_2O$. Zinc corrodes by formation of carbonate, hydroxide, and oxychloride, but from brass is preferentially removed as chloride ("dezincification").

Miethe and Stammreich have reported that mercury, originally free from gold, after prolonged use in a mercury-vapour lamp can be shown to contain small traces of gold which they believe to have been formed by atomic breakdown of mercury.[37] Further details have now been given of the tests applied to detect gold, depending primarily upon separation of the bulk of the mercury by distillation: the residual drop of mercury is dissolved in nitric acid and the gold remaining is estimated by measuring the size of the spherical crystal aggregate under the microscope. It is claimed that it is thus possible to detect 1×10^{-6} mg. of gold in 1 kg. of mercury.[38] The atomic weight of gold so obtained has been estimated and found to be the same as that of ordinary gold,[39] although it has been stated that gold, if obtainable by the transmutation of mercury, should have an atomic weight not less than 198.[39a] These experiments receive confirmation by the independent observation that when a condensed discharge at 600,000 volts is passed between electrodes of mercury and tungsten wire immersed in hydrocarbon oils, the resulting viscous mass of carbon, oil, mercury, etc., can be made to yield ruby glass and is therefore held to contain gold which was not present in the original mercury.[40] Under other conditions, both gold and a complex white metal containing much silver were formed.

[34] R. C. Burt, *J. Opt. Soc. Amer.*, 1925, **11**, 87; *A.*, ii, 921.
[35] Grandadam, *Compt. rend.*, 1925, **180**, 1598; *A.*, ii, 704.
[36] G. D. Bengough and R. May, *J. Inst. Metals*, 1924, **32**, 81; *A.*, 1925, ii, 218.
[37] A. Miethe and H. Stammreich, *Naturwiss.*, 1924, **12**, 597; *Ann. Reports*, 1924, **21**, 35.
[38] H. Stammreich, *Z. anorg. Chem.*, 1925, **148**, 93; *A.*, ii, 1208.
[39] O. Hönigschmid and E. Zintl, *ibid.*, 1925, **147**, 262; *A.*, ii, 924.
[39a] F. W. Aston, *Nature*, 1925, **116**, 208; *A.*, ii, 833.
[40] H. Nagaoka, *Nature*, 1925, **116**, 95; *J. Phys. Radium*, 1925, [vi], **6**, 209; *A.*, ii, 835, 1111.

A claim for priority in the transmutation of mercury into other elements has been made by Gaschler,[41] who states that repeated passage of momentary high-tension discharges between tungsten electrodes in a silica tube containing mercury and uranium oxide results in increased radioactivity due to the production of uranium-*X*.

Group II.

Pure metallic beryllium has been prepared by electrolysis of a fused mixture of sodium beryllium fluoride and barium beryllium fluoride. This electrolyte is maintained at 1350° in an Acheson graphite crucible which serves as anode, the cathode being an iron rod, water-cooled internally, to which the beryllium adheres. Chiefly because of the volatility of the fluorides at the high temperature necessary for electrolysis, the yield of metal is low (45—50%), but it is obtained in a compact, crystalline form, $d^{18°}$ 1·842, containing but traces of sodium or barium and little or no iron: freedom from other metallic impurities is attained if they are excluded from the electrolyte. Relatively large quantities of pure beryllia are conveniently prepared for this purpose by a process involving solution in aqueous sodium bicarbonate and reprecipitation as basic beryllium carbonate.[42] Vapour pressure measurements for hydrated beryllium sulphate indicate that only the tetra- and di-hydrates, and possibly the monohydrate, exist: no evidence could be found for the existence of the hexa- and hepta-hydrates described in the literature.[43]

Magnesia dissolves to a small extent (0·1%) in mixtures of magnesium fluoride with alkali and alkaline-earth fluorides molten at 750—950°, and electrolysis of the melt yields metallic magnesium of relatively high purity and, in particular, free from hygroscopic impurities such as lead to rapid corrosion. Apparently the primary action is electrolysis of magnesium fluoride, but this compound is regenerated by reaction between the liberated fluorine and magnesia dissolved in the melt.[44]

Some interesting experiments may be recorded upon the use of a zinc arc as a means of reduction. If a direct-current arc is maintained between a zinc anode and carbon cathode immersed in liquid carbon disulphide at 0°, a considerable yield of carbon subsulphide, about 50% of that expected according to the reaction $3CS_2+4Zn \longrightarrow$

[41] A. Gaschler, *Nature*, 1925, **116**, 396; *A.*, ii, 925.

[42] A. Stock, P. Praetorius, and O. Priess, *Ber.*, 1925, **58**, [*B*], 1571; *A.*, ii, 1090.

[43] F. Krauss and H. Gerlach, *Z. anorg. Chem.*, 1924, **140**, 61; *A.*, 1925, ii, 314.

[44] W. G. Harvey, *Trans. Amer. Electrochem. Soc.*, 1925, **47**, 229; O. Ruff and W. Busch, *Z. anorg. Chem.*, 1925, **144**, 87; *A.*, ii, 570, 569.

$C_3S_2 + 4ZnS$, is obtained. With silicon tetrachloride at $-55°$ to $-15°$, using an aluminium cathode, the zinc arc produces mainly silicon with some hexachlorodisilane (m. p. $+2{\cdot}5°$), and under similar conditions phosphorus trichloride yields mainly yellow phosphorus with some dichloride, P_2Cl_4, m. p. $-28°$, whilst boron trichloride gives chiefly boron with a small quantity of a new chloride, B_2Cl_4, m. p. $-100°$, b. p. $0°/44$ mm. This chloride decomposes slowly at the ordinary temperature into boron and boron trichloride, yields with water a fairly stable compound containing the B·B group, and with aqueous sodium hydroxide gives hydrogen according to the scheme $B_2Cl_4 + 3H_2O \longrightarrow B_2O_3 + 4HCl + H_2$. As these effects are profoundly modified by the use of alternating current, they are not solely attributable to the reducing action of zinc vapour at arc temperatures.[45]

When excess of hydrogen peroxide is added to aqueous baryta below 20°, the white, crystalline hydrate, $BaO_2,8H_2O$, first formed changes to a buff-coloured, granular precipitate which, on drying in a vacuum over phosphoric oxide, becomes a cream or buff-coloured, non-crystalline powder. This substance decolorises potassium permanganate more rapidly than does barium dioxide, it liberates iodine from potassium iodide and bromine from potassium bromide in presence of nitric acid, and it reacts vigorously with sulphur but without formation of sulphur dioxide. It does not contain hydrogen peroxide, as this substance can be detected neither in the moisture liberated from the solid on heating nor in the ethereal extract of the solid. Analyses by decomposition of the solid at 500—600° in nitrogen and by titration with permanganate in nitric acid solution show that the atomic ratio of oxygen to barium is very approximately 3 : 1; hence it is apparently a new peroxide of the formula BaO_3.[46]

Further work has confirmed the existence of calcium carbonate hexahydrate ($d^{15°}$ 1·789). It is formed by the action of atmospheric carbon dioxide on sugar–lime solutions, is stable in such solutions below 10·4°, and above that temperature changes to a pentahydrate ($d^{15°}$ 1·834), stable between 10·4° and 17°. No evidence was obtained of the existence of lower hydrates and it appears that above 17° anhydrous calcium carbonate is the only stable phase.[47]

An interesting observation has been recorded, applicable to the rapid estimation of many metals dissolved in mercury and, more important, affording a rapid and efficient means of purifying mercury from such metals. In the latter operation a reasonable excess of

[45] A. Stock, A. Brandt, and H. Fischer, *Ber.*, 1925, **58**, [*B*], 643; *A.*, ii, 570.
[46] (Miss) M. Carlton, *J.*, 1925, **127**, 2180; compare *Ann. Reports*, 1921, **18**, 44.
[47] J. Hume, *J.*, 1925, **127**, 1036.

the oxidising agent is used and thus such metals as zinc, manganese, cadmium, thallium, tin, lead, copper, chromium, iron, and bismuth are rapidly eliminated without loss of mercury. For example, by shaking with a concentrated solution of permanganate in 6*N*-sulphuric acid containing a little ferric sulphate, 14 grams of a mixture of zinc, cadmium, tin, lead, solder, and bismuth were completely removed from 480 grams of mercury, without loss of the latter, whilst shaking with a normal solution of ferric sulphate in 2*N*-sulphuric acid removed 7 grams of zinc from 200 grams of amalgam in 30 seconds.[48]

Group III.

In the course of a critical examination of methods of preparing boron, it has been found that "Moissan's boron," prepared by reducing boric oxide with magnesium, is a mixture of boron with a new oxide, B_3O. Pure amorphous boron was obtained in small yield by electrolysing a fused mixture of potassium carbonate, potassium chloride, and boron trioxide, using a carbon anode and a copper cathode, and fused boron by reducing Moissan's boron with aluminium at arc temperatures. Boron was found to replace gold, platinum, palladium, silver, mercury, copper, and lead from their solutions, and hence, in the electrochemical series, occupies a position just above lead.[49] Alkali borates have been prepared of a new type distinct from those previously known (MBO_2, $M_2B_4O_7$, $M_2B_{10}O_{16}$, $M_2B_8O_{13}$, and, probably, $M_2B_6O_{10}$). Solutions of potassium tetraborate with excess of boric acid sufficient to give a ratio B : K : : 2·5 : 1 yield at 115—120° microcrystalline prisms of the new pentaborate, $K_2HB_5O_9,2H_2O$, which is more readily obtained by heating concentrated aqueous potassium tetraborate at 115—120° in a sealed tube and seeding the solution with the pentaborate. The corresponding sodium salt is easily obtained by simple heating of borax and water at 115° in a sealed tube.[50]

Gallium sulphate, $Ga_2(SO_4)_3,18H_2O$, has been found to be stable in air : the hydroxide is distinctly more acidic and less basic than aluminium hydroxide. Solubility curves for gallium hydroxide in sodium hydroxide show a maximum at about 10·3*N*-sodium hydroxide, indicating the existence of trisodium gallate and mono- or di-sodium gallate as distinct phases, of which the former is soluble and the latter insoluble in water.[51]

[48] A. S. Russell and D. C. Evans, *J.*, 1925, **127**, 2221.

[49] H. H. Kahlenberg, *Trans. Amer. Electrochem. Soc.*, 1925, **47**, 59; *A.*, ii, 425.

[50] V. Auger, *Compt. rend.*, 1925, **180**, 1602; *A.*, ii, 697.

[51] R. Fricke and W. Blencke, *Z. anorg. Chem.*, 1925, **143**, 183; *A.*, ii, 417.

Earlier work having shown that thallium existed in two enantiotropic forms and that the transformation of α- into β-thallium was accompanied by an abrupt change in the *X*-ray pattern, this observation was applied to redetermine the transition point, 231·3°. Later investigation of the transition point by the thermal method using very pure electrolytic thallium gave the slightly higher value 232·5° ± 0·5°, which is preferred.[52]

The technique devised in attempts to separate isotopes by the ionic migration method has been developed and applied to the separation of rare-earth mixtures. A 2% agar-agar gel containing a given mixture (0·5 *N*) is placed in a long glass tube between similar gels containing a faster kation ($K^{\cdot}$) nearer the cathode and a slower kation ($Cr^{\cdot\cdot}$) nearer the anode. On electrolysis, the more mobile rare-earth kation accumulates in the forward portion of the tube, and the gel is then cut into slices and analysed. In three typical mixtures, yttrium–erbium, neodymium–praseodymium, and gadolinium–samarium, a very good separation was thus effected; with the first pair, a long tube being used and the electrolysis continued for 21 days, the purest fraction contained 99% of yttrium.[53]

Pure metallic praseodymium has been prepared by electrolysis of the fused chloride, using a low current density. The praseodymia was prepared from cerium earth residues, several known procedures being used for fractionation, of which the best was found to be fractional crystallisation of the double magnesium and manganese nitrates; the final product probably contained less than 0·3% of impurity, chiefly neodymium and lanthanum. Praseodymium is a silver-white metal, corrodes rapidly in air, and is attacked slightly by hot water and vigorously by free halogens and mineral acids; it has $d^{25°}$ 6·60, kindles in air at 290°, but is not pyrophoric.[54] Metallic neodymium of moderate purity was obtained by electrolysis of the fused chloride containing a little sodium chloride; the first product of electrolysis was the subchloride, $NdCl_2$, which was subsequently reduced to the metal. Neodymium resembles praseodymium closely in appearance and in its reactions with air, water, and acids; it has $d^{15°}$ 7·05 and kindles in air at 270°; it alloys readily with iron, aluminium, nickel, and copper.[55] Metallic cerium, free from iron, was obtained by electrolysing the fused chloride in graphite cells with carbon anodes. It is very malleable

[52] G. Asahara, *Sci. Papers, Inst. Phys. Chem. Res. Tokyo*, 1925, **2**, 125, 253; *A.*, ii, 483, 645.

[53] J. Kendall and B. L. Clarke, *Proc. Nat. Acad. Sci.*, 1925, **11**, 393; *A.*, ii, 977.

[54] J. Wierda and H. C. Kremers, *Trans. Amer. Electrochem. Soc.*, 1925, **48**, 65; *A.*, ii, 993.

[55] H. C. Kremers, *ibid.*, 1925, **47**, 221; *A.*, ii, 588.

and ductile, moderately pyrophoric, and corrodes easily in dry air; it has $d^{15°}$ 6·77; Brinell hardness (500 kg.) 21; heat of combustion 1·661 Cal./g.; kindling temperature 165°.[56]

Group IV.

Colourless diamond has been found to have a heat of combustion 7873 ± 4 Cal./g. as compared with 7884 ± 2 for carbonado, 7856 ± 1 for β-graphite, and 7832 ± 1 for α-graphite, whence it would appear, contrary to earlier results,[57] that at the ordinary temperature white diamond is a less stable form than graphite. The relatively high value for carbonado may be explained on the assumption that it consists of white diamond containing a proportion of amorphous carbon having a heat of combustion of about 8060 Cal./g.[58] The transformation of diamond into graphite at high temperatures is comparatively slow in a vacuum, being incomplete in an hour at 1500—1900°, in marked contrast with the rapid change in presence of gases; it occurs more rapidly at 2000°, although sometimes without the swelling and disintegration observed in gaseous atmospheres, and the rate differs greatly for different specimens.[59]

Further pursuit of experiments previously reported [60] has afforded strong evidence that carbon can be fused at atmospheric pressure. Carbon rods 99·9% pure and constricted in the middle were heated electrically in an atmosphere of argon and observed by means of a kinematograph camera. As the current was increased, no gradual diminution of the cross section of the rod occurred, but a bright line suddenly appeared at the narrowest part, where, less than 0·1 second later, the rod parted and formed an arc. Afterwards, small globules, of equal density, were found in the vicinity of the arc, whence it seems clear that the rod parted by fusion and not by sublimation. The temperature of the rod at the moment of parting, measured by a radiation pyrometer, was independent of the pressure between 0·21 and 0·935 atm., and this value, 3800° ± 100° Abs., was taken as the melting point. The temperature of the arc formed was found to depend on the pressure, varying from 3450° Abs. at 0·005 atm. to 4330° Abs. at 1·5 atm., and these values above 3800° Abs. are believed to represent the boiling point of graphite at different

[56] H. C. Kremers and H. Beuker, *Trans. Amer. Electrochem. Soc.*, 1925, **47**, 213; *A.*, ii, 581.
[57] Berthelot and Petit, *Ann. Chim. Phys.*, 1889, **18**, 80.
[58] W. A. Roth and W. Naeser, *Z. Elektrochem.*, 1925, **31**, 461; *A.*, ii, 1140.
[59] P. Lebeau and M. Picon, *Compt. rend.*, 1924, **179**, 1059; *A.*, 1925, ii, 136.
[60] *Ann. Reports*, 1922, **19**, 49.

temperatures.[61] This value for the melting point of carbon has been independently confirmed by another method yielding the value 3760° ± 65° Abs.[62]

More detailed röntgenographic examination of amorphous carbons indicates that, contrary to previous conclusions, amorphous carbon is a true modification distinct from graphite.[63]

The vapour-pressure curve of carefully purified hydrogen cyanide has been determined, in one case [64] from 0° to 46°, in another [65] from − 15° to 180°. In the latter case, the critical constants, $T_c = 183{\cdot}5° \pm 0{\cdot}1°$, $P_c = 53{\cdot}2 \pm 0{\cdot}5$ atm., $d_c = 0{\cdot}195$, were also determined, whence the molecular latent heat of evaporation is calculated as 6·76 kg.-cal. at 25·6° (b. p.) and 7·22 kg.-cal. at − 13·4° (m. p.).

Surface "devitrification" of fused silica vessels and tubing is well known to occur in use; eventually the change proceeds so far that the ware becomes fragile and useless. It is, therefore, of considerable practical interest to know that it is due to a transformation, probably to cristobalite, which is greatly hastened by the presence of crystal nuclei or "slag" particles and can be prevented or greatly minimised if, as soon as the change becomes noticeable, the corroded surface layer is removed by momentary immersion in aqueous hydrofluoric acid containing a little sulphuric acid. Silica thus treated becomes clear and smooth and its useful life is prolonged.[66]

The properties of monogermane have been further investigated: it has m. p. − 165°, b. p. − 90°, and its density as liquid at − 142° is 1·523. Analysis has confirmed the formula GeH_4, and the normal litre of the gas weighs 3·420 grams. It decomposes into germanium and hydrogen at about 280°.[67] Independent determinations upon monogermane prepared by electrolysis of a sulphuric acid solution of germanium dioxide with lead electrodes and purified by condensation with liquid air and fractionation in Stock's

[61] E. Ryschkewitsch, *Z. Elektrochem.*, 1925, **31**, 54; *A.*, ii, 276; see also H. Kohn and M. Guckel, *Z. Physik*, 1924, **27**, 305; K. Fajans, *Z. Elektrochem.*, 1925, **31**, 63; *A.*, ii, 100, 277.

[62] H. Alterthum, W. Fehse, and M. Pirani, *ibid.*, 1925, **31**, 313; *A.*, ii, 759.

[63] O. Ruff, G. Schmidt, and W. Olbrich, *Z. anorg. Chem.*, 1925, **148**, 313; *A.*, 1925, ii, 1125.

[64] R. Hara and H. Sinozaki, *Tech. Rep. Tôhoku Imp. Univ.*, 1924, **4**, 145; *A.*, ii, 279.

[65] G. Bredig and L. Teichmann, *Z. Elektrochem.*, 1925, **31**, 449; *A.*, ii, 950.

[66] F. C. Vilbrandt, *Ind. Eng. Chem.*, 1925, **17**, 835; *A.*, ii, 1091.

[67] R. B. Corey and A. W. Laubengayer (with L. M. Dennis), *J. Amer. Chem. Soc.*, 1925, **47**, 112; *A.*, ii, 493.

apparatus confirm the foregoing data (b. p. — 88·5°, m. p. — 164·5°, mol. heat of evaporation 3·65 kg.-cal.;[68] b. p. — 90° to — 91°).[69]

Germanium glasses of four types, a very dense flint, a flint, a borate crown, and a barium crown glass, have been prepared and compared in each case with a corresponding silicate glass in which germanium dioxide was replaced by an equimolecular proportion of silica. The germanium glasses closely resemble the silicate glasses except that the former have higher refractive indices and, as they melt at considerably lower temperatures, can more easily be obtained homogeneous and free from air bubbles.[70]

Tin hydride has been obtained in a state of fair purity (99·7%) by electrolysing a solution of tin sulphate between lead electrodes with the addition of certain colloids (*e.g.*, 0·5% of dextrin) to the electrolyte, whereby the yield is increased and the product stabilised. The maximum concentration of hydride thus obtained in the evolved hydrogen is about 0·01%, but after the gas has been washed with water and alkaline lead acetate solution, and dried by passage through tubes cooled to — 80° to — 100°, the tin hydride may be condensed in liquid air and purified by fractional distillation and fractional condensation at low temperatures. The hydride is relatively stable at the ordinary temperature, decomposing only after some days in glass vessels, but it is very sensitive and is decomposed rapidly at ground glass joints, at tin mirrors (even when these are invisible to the naked eye), and in contact with calcium chloride and phosphoric oxide. It decomposes rapidly and completely at about 150°, and it has thus been analysed and shown to have the formula SnH_4. The solid hydride melts at — 150° (± 2°). The gas does not react with aqueous alkali hydroxides (up to 15%), dilute sulphuric acid, dilute or concentrated nitric acid, sodium carbonate, copper sulphate, ferric chloride, or lead acetate, but is absorbed partly by concentrated sulphuric acid and strong aqueous alkali hydroxides and completely by solid alkali hydroxides, soda-lime, and aqueous silver nitrate. In the last case, a black precipitate is formed containing both tin and silver.[71]

Reference may here be made to an interesting general discussion of the group of volatile hydrides, of which the foregoing are members, where it is held that the close physical similarity of these

[68] F. Paneth and E. Rabinovitsch, *Ber.*, 1925, **58**, [*B*], 1138; *A.*, ii, 760.

[69] R. Schenk and A. Imker, *ibid.*, 1925, **58**, [*B*], 271; *A.*, ii, 279.

[70] L. M. Dennis and A. W. Laubengayer, *J. Amer. Chem. Soc.*, 1925, **47**, 1945; *A.*, ii, 888.

[71] F. Paneth and E. Rabinovitsch, *Ber.*, 1924, **57**, [*B*], 1877; F. Paneth, W. Haken, and E. Rabinovitsch, *ibid.*, 1924, **57**, [*B*], 1891; *A.*, 1925, ii, 59, 60.

hydrides to the rare gases indicates that the hydrogen nuclei are "buried" in the molecule, which, therefore, presents a "rare-gas" surface.[68]

A good deal of work has been done on zirconium and hafnium. These metals (and also titanium and thorium) are deposited in thick layers on a tungsten filament heated in the vapour of the appropriate iodide; it is stated that hafnium is denser than zirconium, and has a higher melting point and a higher electron emission.[72] Zirconium and hafnium phosphates precipitated from 6*N*-hydrochloric acid have the composition $MO(H_2PO_4)_2$;[73] they are soluble in concentrated sulphuric or phosphoric acid and in oxalic acid and are reprecipitated on dilution or in the last case on addition of alcohol or mineral acids; the solutions of hafnium phosphate are the less stable, and fractional precipitation as phosphate constitutes an important step in the separation of hafnium and zirconium.[74] These phosphates are also easily soluble in hydrofluoric acid and a method for separating hafnium and zirconium has been based on this fact.[75] Further purification is in some cases effected by fractional solution in saturated sodium carbonate solution.[76] A better method appears to be fractionation as ammonium and potassium double fluorides; by warming the crude dioxides with ammonium fluoride and hydrofluoric acid, double fluorides of the type $(NH_4)_3RF_7$ are obtained which are unsuitable for fractionation; these are therefore converted into the fluorides $(NH_4)_2RF_6$ (R = Zr, Hf), which are fractionally crystallised until the hafnium content, originally 2—5%, is raised to 38%. Subsequently fractionation by recrystallisation of the potassium salts, K_2RF_6, may be made to yield a hafnium salt of more than 99·9% purity; in all these cases the hafnium salt is the more soluble.[77] Another interesting method of separation has been proposed depending upon fractional distillation of the compounds $2RCl_4,PCl_5$: the zirconium compound, previously de-

[72] A. E. van Arkel and J. H. de Boer, *Z. anorg. Chem.*, 1925, **148**, 345; *A.*, ii, 1193.

[73] G. Hevesy and K. Kimura, *J. Amer. Chem. Soc.*, 1925, **47**, 2540; *A.*, ii, 1147.

[74] J. H. de Boer and A. E. van Arkel, *Z. anorg. Chem.*, 1925, **148**, 84; *A.*, ii, 1185.

[75] *Idem, ibid.*, 1925, **144**, 190; *A.*, ii, 705.

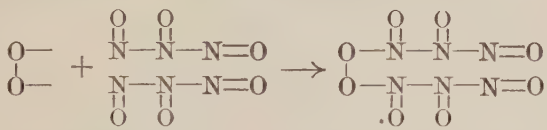
[76] (Mlle.) M. Marquis, P. Urbain, and G. Urbain, *Compt. rend.*, 1925, **180**, 1377; J. Bardet and C. Toussaint, *ibid.*, 1925, **180**, 1936; *A.*, ii, 699, 826.

[77] J. H. de Boer and A. E. van Arkel, *Z. anorg. Chem.*, 1924, **141**, 284; G. von Hevesy and E. Madsen, *Z. angew. Chem.*, 1925, **38**, 228; G. von Hevesy, J. A. Christiansen, and V. Berglund, *Z. anorg. Chem.*, 1925, **144**, 69; *A.*, ii, 243, 425, 505; see also Naamlooze Venootschap Philips' Gloeilampenfabriken, Fr. Pats. 568978 and 569016.

scribed,[78] is a white, crystalline solid, m. p. 164·5°, b. p. 416°, readily hydrolysed to form a compound, $2ZrCl_4,POCl_3$; this is a vitreous solid, b. p. 363—364°, which can easily be reconverted into the former compound by the action of phosphorus pentachloride. Hafnium forms analogous but rather more volatile compounds, and thus, by repeated distillations, can be concentrated in the head fractions: titanium and silicon chlorides are much more volatile, whilst iron and aluminium form additive compounds much less volatile than those of hafnium and zirconium; hence these impurities are eliminated at an early stage of the fractionation.[79]

Group V.

When nitric oxide is bubbled through liquid oxygen, or air acts on solid nitric oxide at — 185°, a green solid is formed which at a slightly higher temperature is converted into a blue solid; analysis shows this to be the oxide N_2O_3.[80] It is now reported that the green solid is a new oxide of nitrogen, *nitroso-nitrogen trioxide*, $(N_3O_4)_x$. The conversion of this oxide into nitrogen trioxide is apparently irreversible and it is assumed, because of its instability and its instantaneous formation, that it is a peroxidised polymeride of nitric oxide produced according to the scheme:



A similar explanation may be applied to the phenomena observed in the oxidation of nitric oxide at higher temperatures, supposing $(NO)_2$ to yield O:N·NO·O·O·NO·N:O and NO to yield O:N·O·O·N:O.[81]

The nitric oxide compound of ferrous selenate, the selenium analogue of that responsible for the "brown ring" test, is obtained by saturating with nitric oxide concentrated aqueous ferrous selenate ($FeSeO_4,5H_2O$) containing a little selenic acid. On cooling and adding a large excess of absolute alcohol saturated with nitric oxide, brownish-black crystals are obtained, apparently having the formula $FeSeO_4,NO,4H_2O$, which are unstable and lose nitric oxide when kept in air.[82]

[78] Payküll, *Ber.*, 1879, **12**, 1719.

[79] A. E. van Arkel and J. H. de Boer, *Z. anorg. Chem.*, 1924, **141**, 289; *A.*, 1925, ii, 243.

[80] D. Helbig, *Atti R. Accad. Lincei*, 1903, **5**, 166; *A.*, 1903, ii, 361. This blue solid was also said, erroneously, to be N_3O_4; F. Raschig, *Chem.-Ztg.*, 1911, **35**, 1096; *A.*, 1912, ii, 346.

[81] R. L. Hasche, *J. Amer. Chem. Soc.*, 1925, **47**, 2143; *A.*, ii, 988.

[82] W. Manchot and E. Linckh, *Z. anorg. Chem.*, 1924, **140**, 37; *A.*, 1925, ii, 317.

Three independent investigations confirm the view that the thermal decomposition of nitrogen pentoxide is a true unimolecular reaction; the temperature coefficient is very large (300% velocity increase for 10° rise), hence there is probably no wall effect, and there is no evidence that the reaction is autocatalytic.[83]

An extremely interesting paper on the constitution of nitric acid must be inadequately summarised: consideration of absorption spectra and electrical conductivity leads to the view that strong nitric acid is an equilibrium mixture of the pseudo-acid $O_2N{\cdot}OH$, the true acid present as the hydroxonium salt, $(NO_3)[H{\cdot}OH_2]$, and the salt-like electrolyte nitronium nitrate, $(NO_3)_2[(HO)_3N]$, the proportion of the second-named being negligible in almost anhydrous nitric acid. The conception of nitronium salts is strengthened by the fact that mixtures of almost anhydrous nitric and perchloric acids deposit *nitronium diperchlorate*,

$$(ClO_4)_2[(HO)_3N],$$

m. p. 130° with decomposition, and *nitronium monoperchlorate*, $ClO_4[(HO)_2NO]$, decomposing above 130°, as stable salts which can be crystallised from perchloric acid and nitric acid, respectively. The reactions between perchloric, sulphuric, and nitric acids, of which the foregoing are typical, are held to afford strong evidence for the chemical theory of acids according to which their strength (acidity) is measured by their tendency toward salt formation and not by their ability to furnish hydrogen ions.[84]

The previously unknown nitrides of zirconium, niobium, scandium, and erbium have been prepared by heating the corresponding oxides with the calculated quantity of carbon at 1250° in nitrogen; they are solids of high melting point.[85]

Nitrogen tetraselenide, prepared by passing a rapid stream of ammonia gas through a cooled solution of selenium monochloride in carbon disulphide and allowing the resultant solution to evaporate, was used for a determination of molecular weight by the cryoscopic method in glacial acetic acid, whence the formula is N_4Se_4. Nitrogen tetrasulphide was obtained in good yield from sulphur monochloride by a similar method, and both sulphides were observed to yield, on prolonged treatment with ammonia, dark coloured liquids, presumably additive compounds, characterised by a most offensive odour.[86] Sublimation of nitrogen sulphide containing free sulphur

[83] H. S. Hirst, *J.*, 1925, **127**, 657; E. C. White and R. C. Tolman, *J. Amer. Chem. Soc.*, 1925, **47**, 1240; J. K. Hunt and F. Daniels, *ibid.*, 1925, **47**, 1602; *A.*, ii, 554, 682, 801.

[84] A. Hantzsch [with L. Wolf], *Ber.*, 1925, **58**, [*B*], 941; *A.*, ii, 634.

[85] E. Friederich and L. Sittig, *Z. anorg. Chem.*, 1925, **143**, 293; *A.*, ii, 419.

[86] H. B. van Valkenburgh and J. C. Bailar, *J. Amer. Chem. Soc.* 1925 **47**, 2134; *A.*, ii, 993.

over silver gauze at about 125° yields a film of a ruby-red compound which on keeping or at 50° turns deep blue and behaves as blue nitrogen sulphide; in the absence of sulphur, the blue compound only is obtained. Sublimation of nitrogen sulphide with sulphur at 125° in the absence of silver gauze produced small quantities of a dark red, easily volatile liquid, resembling bromine and having an odour like that of iodine; it formed a pale yellow solid at — 80° and on analysis by decomposition gave data corresponding with the formula NS_2; it is therefore regarded as a new *nitrogen persulphide*.[87]

Dry bromine vapour reacts with sodium or silver azide, giving bromoazoimide, N_3Br. This substance is extremely unstable, decomposing explosively on shock in all states of aggregation and even at — 200°; it melts at about — 45°. Bromoazoimide is instantly hydrolysed by water, consequently bromine water reacts with sodium azide to form sodium bromide, azoimide, and hypobromous acid, and these further react, forming nitrogen. Hypobromous acid reacts even more rapidly with sodium azide, so that two equivalents of bromine are able to decompose two equivalents of sodium azide.[87a]

Extension of work previously reported [88] has shown that the spectrum of the glow of phosphorus trioxide is identical with that of the glow of phosphorus and that the burning of hydrogen phosphide in air shows the same ultra-violet bands with certain differences in intensity. From these and other facts it is inferred that low-temperature combustion of phosphorus, the trioxide, and the trihydride involves a common stage responsible for the chemical anomalies and intimately associated with the characteristic light-emission.[89]

Group VI.

Further physical constants of ozone have been determined as follows: m. p. — 251·4°, b. p. — 112·3°, critical temperature — 5°, critical pressure (calculated) 67 atm., critical density 0·54, critical volume 89·4 c.c./mol., density of liquid at — 183° 1·71 ± 0·05; the critical solution temperature of liquid ozone and liquid oxygen is — 158°.[90] It has been found that appreciable quantities of ozone, much in excess of those to be anticipated by thermal formation, are produced by passing dry oxygen through quartz capillaries

[87] F. L. Usher, *J.*, 1925, **127**, 730.

[87a] D. A. Spencer, *J.*, 1925, **127**, 216.

[88] *Ann. Reports*, 1924, **21**, 46.

[89] H. J. Emeléus, *Nature*, 1925, **115**, 460; *J.*, 1925, **127**, 1362; *A.*, ii, 354, 740.

[90] G. M. Schwab, *Z. physikal. Chem.* 1924, **110**, 599; *A.*, 1925, ii, 149.

at 750—1250°, and that presence of moisture reduces the yield of ozone. This confirms the view that hydrogen peroxide plays no part in ozone formation.[91]

Because the provision of a convenient supply of hydrogen sulphide is a perennial laboratory problem, it seems worth while to direct attention to the fact that a copious supply may be obtained by gently heating a mixture of sulphur and paraffin wax; the generation of gas ceases almost immediately on withdrawing the source of heat and when a charge is spent it may easily be renewed if the precaution is taken to mix the materials originally with ignited asbestos.[92] A number of compounds of metallic halides with hydrogen sulphide, named "thiohydrates," have been proved to exist and are formulated as follows: $BeBr_2,2H_2S$; $BeI_2,2H_2S$; $AlCl_3,H_2S$; $AlBr_3,H_2S$; $AlI_3,2H_2S$; $AlI_3,4H_2S$; $TiCl_4,H_2S$; $TiCl_4,2H_2S$; $TiBr_4,H_2S$; $TiBr_4,2H_2S$; $SnCl_4,2H_2S$; $SnCl_4,4H_2S$.[93]

Whilst it has long been known that sulphur reacts with sulphur trioxide to produce a bluish-green solid and a blue liquid and Weber[94] found the sulphur content of the bluish-green solid to correspond with the formula S_2O_3, it has latterly been generally believed that the supposed sulphur sesquioxide was a "colloidal solution." It has now been found that on adding pure redistilled sulphur to pure sulphur trioxide under careful exclusion of moisture, a violent reaction sets in after 30 seconds and a bluish-green solid is formed. The excess of sulphur trioxide may be removed by distillation in a vacuum at 30—40°, and, although the substance begins to decompose after a few minutes at 15°, it was possible by two distinct methods of analysis to prove that the sulphur content was that required by the formula S_2O_3 and hence that sulphur sesquioxide does exist. It is at once decomposed by water, with deposition of sulphur and formation of sulphuric, sulphurous, tri-, penta-, and possibly tetra-thionic acids. With sodium ethoxide in alcoholic solution, it forms sodium ethyl sulphoxylate, $NaEtSO_2$, which on hydrolysis yields sodium sulphoxylate as a white, crystalline solid moderately soluble in cold water and sparingly soluble in alcohol, and practically unattacked by boiling concentrated sulphuric and hydrochloric acids.[95] The production of thionic acids from sulphur sesquioxide and the known reactions and properties

[91] E. H. Riesenfeld, *Z. Elektrochem.*, 1925, **31**, 435; *A.*, ii, 989 (compare *Ann. Reports*, 1924, **21**, 48; E. H. Riesenfeld, *Z. physikal. Chem.*, 1924, **110**, 801; H. von Wartenburg, *ibid.*, 1924, **110**, 285; *A.*, 1925, ii, 148, 147).

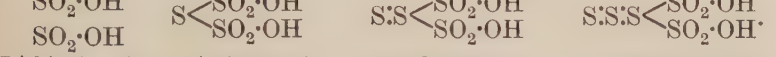
[92] A. Henwood, R. M. Carey, W. Goldberg, and E. Field, *J. Franklin Inst.*, 1925, **199**, 685; *A.*, ii, 705.

[93] W. Biltz and E. Keunecke, *Z. anorg. Chem.*, 1925, **147**, 171; *A.*, ii, 986.

[94] Weber, *Ann. Phys. Chem.*, 1875, **156**, 531.

[95] I. Vogel and J. R. Partington, *J.*, 1925, **127**, 1514.

of these acids and their salts have led to the following formulæ : [96]



Dithionic acid. Trithionic acid. Tetrathionic acid. Pentathionic acid.

Solubility determinations for sodium and potassium sulphites prepared and handled in an atmosphere of hydrogen give no evidence for the existence of $NaHSO_3$ or $KHSO_3$, but show that only pyrosulphites crystallise from acid solutions. Potassium pyrosulphite is anhydrous at all temperatures and sodium pyrosulphite in equilibrium with its solution is anhydrous down to 5·5° and below that temperature may form a stable phase with 7 mols. of water or a metastable phase with 6 mols. of water. The thermal decomposition of calcium, sodium, and magnesium sulphites has also been studied in some detail.[97] Work on the decomposition of polythionates in aqueous solution, on the influence of thiosulphate and sulphite on their stability, and on the action upon them of alkali and hydrogen sulphide can only be referred to here.[98]

Selenium monochloride and monobromide have hitherto been prepared in absence of water, with the attendant experimental complications, but it is now shown that these compounds may easily be prepared in quantity by dissolving the dioxide in the appropriate halogen acid and adding the requisite quantity of elementary selenium. Gradual addition of excess of concentrated sulphuric acid then precipitates the selenium monohalide as an oil which can be separated and purified in the usual manner : the yield is 90%.[99] Careful comparison of properties shows that the compounds of selenium dioxide with the halogen acids, $SeO_2,2HCl$ and $SeO_2,2HBr$, are identical with the hydrates $SeOCl_2,H_2O$ and $SeOBr_2,H_2O$: the latter compound is obtained as a reddish-brown oil when hydrogen bromide is passed over selenium dioxide; it has $d^{22°}$ 3·077; at 115°, it begins to decompose, yielding bromine, selenium monobromide, tetrabromide, and oxybromide, selenium dioxide, water, and hydrogen bromide. On cooling the liquid to — 10°, red selenium tetrabromide crystallises out; on addition of selenium dioxide, yellow needle crystals of $SeOBr_2$, m. p. 40°, are

[96] I. Vogel, *J.*, 1925, **127**, p. 2248.

[97] F. Foerster, A. Brosche, and C. Norberg-Schulz, *Z. physikal. Chem.*, 1924, **110**, 435; F. Foerster and K. Kubel, *Z. anorg. Chem.*, 1924, **139**, 261; *A.*, 1925, ii, 120.

[98] A. Kurtenacker and M. Kauffmann, *Z. anorg. Chem.*, 1925, **148**, 43, 225, 256, 369; *A.*, ii, 1189, 1190.

[99] V. Lenher and C. H. Kao, *J. Amer. Chem. Soc.*, 1925, **47**, 772; *A.*, ii, 426.

obtained, but stronger dehydrating agents, such as sulphuric acid, precipitate the tetrabromide. Selenium oxychloride may be conveniently prepared by dehydrating the compound $SeO_2,2HCl$ with 70% sulphuric acid: so obtained, it has m. p. 10·9°, b. p. 176°, $d^{22°}$ 2·424.[1]

The usual methods for preparing selenic acid by oxidation of selenious acid with halogen give a product of doubtful purity and involve removal of halogen acid by addition of silver carbonate or some equivalent device.[2] A much simpler and better method is rendered possible by the fact that the selenites of the alkali metals and of barium and strontium are easily converted into selenates by roasting them in air; the preparation of the selenites may be effected in the same operation by starting with a mixture of selenium or selenium dioxide and metallic carbonate. If a solution of potassium selenate is precipitated with a slight excess of perchloric acid and the latter is distilled from the filtrate under reduced pressure, selenic acid of high purity is easily obtained.[3]

Molybdenum pentoxide is obtained by heating the oxysulphate or the oxyoxalate of tervalent molybdenum in a current of nitrogen: $Mo_2O(SO_4)_2 \longrightarrow Mo_2O_5 + 2SO_2$; $Mo_2O(C_2O_4)_2 \longrightarrow Mo_2O_5 + 4CO$.[4] Metallic tungsten has been obtained as powder or as a coherent deposit on copper, nickel, or cobalt, by electrolysis of molten sodium tungstate at 950°, with addition of tungstic oxide, and a detailed study has been made of the binary systems of lithium tungstate with sodium tungstate and potassium tungstate and of tungsten trioxide with each of the foregoing.[5] Complex uranyl carbonates of silver and barium, $Ag_4UO_2(CO_3)_3$ and

$$Ba_2UO_2(CO_3)_3,6H_2O,$$

have been described.[6]

Group VII.

When chlorine dioxide is exposed to light, a dark-red oil is produced reported in one case to be chlorine heptoxide, b. p. about 80°, and in another to be chlorine hexoxide, Cl_2O_6 having a very low vapour pressure, 1 mm. at 20°, $d^{20°}$ 1·65, and m. p. — 1°:[7]

[1] C. W. Muehlberger and V. Lenher, *J. Amer. Chem. Soc.*, 1925, **47**, 1842; *A.*, ii, 890.

[2] V. Lenher and C. H. Kao, *ibid.*, p. 1521; *A.*, ii, 817.

[3] V. Lenher and E. J. Wechter, *ibid.*, p. 1522; *A.*, ii, 815.

[4] W. Wardlaw and F. H. Nicholls, *J.*, 1925, **127**, 1311, 1487.

[5] J. A. M. van Liempt, *Z. Elektrochem.*, 1925, **31**, 249; *Z. anorg. Chem.*, 1925, **143**, 285; *A.*, ii, 694, 421.

[6] J. A. Hedvall, *Z. anorg. Chem.*, 1925, **146**, 225; *A.*, ii, 990.

[7] H. Booth and E. J. Bowen, *J.*, 1925, **127**, 510; M. Bodenstein, P. Harteck, and E. Padelt, *Z. anorg. Chem.*, 1925, **147**, 233; *A.*, ii, 573, 991.

further work on this matter is evidently necessary to reconcile these conflicting conclusions.

Two pseudo-halogens have been obtained as free radicals. Electrolysis of an alcoholic solution of potassium cyanate with a flowing mercury cathode yields a solution containing *oxycyanogen*, $(OCN)_2$, which has not been isolated but in solution has an odour like that of the halogens, liberates iodine from potassium iodide, and dissolves copper, zinc, and iron without evolution of gas. *Selenocyanogen*, $(SeCN)_2$, is prepared by the action of iodine at 10° on excess of silver selenocyanate in ether, chloroform, or carbon tetrachloride; evaporation of the filtered solution yields selenocyanogen as a yellow, crystalline powder exhibiting the properties typical of halogens; it can be preserved in a vacuum, but becomes red in a few hours on exposure to air.[8]

Three allotropic forms of manganese exist, α, β, and γ, of which the β- and γ-forms are present normally in commercial manganese; α-manganese can only be obtained electrolytically, the γ-form is produced when manganese is heated above 850° in a vacuum and suddenly quenched, and the β-form is obtained from γ-manganese by sublimation in a vacuum at 1105°.[9] In the course of investigations on the oxidation of manganous salts to permanganic acid and on the reduction of that acid by arsenious acid, manganic fluoride, orthophosphate, metaphosphate, and orthoarsenate have been described.[10]

Element No. 75, Mendeléeff's "dvi-manganese," has been discovered. Noddack and Tacke state that they have found traces of elements 43 (eka-manganese) and 75 (dvi-manganese) in platinum ores and in columbite and that examination of the *X*-ray spectrum of concentrates derived therefrom indicates the presence of 0·5% and 5%, respectively, of these elements. There seems, however, some doubt whether they have in fact obtained these elements, as the *X*-ray spectra are inconclusive. These observers also report that tantalite and tungstite contain traces of element No. 75 and that sperrylith, gadolinite, fergusonite and zircon contain traces of element No. 43; they propose the names "*rhenium*" and "*masurium*," respectively, for these elements.[11]

Druce and Loring, in the course of a search for element 93 in manganese salts, after an unsuccessful attempt to effect a separation

[8] L. Birckenbach and K. Kellermann, *Ber.*, 1925, **58**, [*B*], 786; *A.*, ii, 568.
[9] A. J. Bradley, *Phil. Mag.*, 1925, [vi], **50**, 1018; *A.*, ii, 1124.
[10] A. Travers, *Bull. Soc. chim.*, 1925, [iv], **37**, 456; *A.*, ii, 585.
[11] W. Noddack and I. Tacke, *Naturwiss.*, 1925, **26**, 567; W. Noddack, I. Tacke, and O. Berg, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1925, 400; *A.*, ii, 939.

by fractional crystallisation, obtained preparations comparatively rich in dvi-manganese from the residual solution left after precipitation of the manganese as sulphide in an ammoniacal solution. The *X*-ray spectrum of the oxide thus obtained, photographed in the research laboratory of Messrs. Adam Hilger, Ltd., gave definite Lα and Lβ lines of element No. 75. Independently Dolejšek and Heyrovský, by polarographic-electro-analysis with a dropping mercury cathode, have obtained evidence of the presence of dvi-manganese in manganese sulphate solutions, and have confirmed the presence of dvi-manganese in the products obtained by Druce and Loring.

These workers, whose priority in publication is admitted by Dolejšek and Heyrovský, prefer the name dvi-manganese to the name "rhenium" proposed by Noddack and Tacke.

As yet, little is known of the chemistry of dvi-manganese except that the sulphide is not precipitated in ammoniacal solution, that the chloride is apparently volatile, that the oxide is insoluble in caustic alkalis though turned brown by them, and that an unstable potassium dvi-manganate can apparently be obtained. Further work on this element will be awaited with keen interest by all chemists.[12]

Group VIII.

By the action of potassamide on cobaltous thiocyanate in liquid ammonia solution *cobaltous amide*, $Co(NH_2)_2$, is obtained and this at 120° loses ammonia to form *cobaltous nitride*, Co_3N_2, as a black solid almost unaffected by water; the action of iron wire on mercuric thiocyanate in the same solvent yields *ferrous tetramminethiocyanate*, $Fe(SCN)_2,4NH_3$, which is converted by potassamide into *ferrous nitride*, Fe_3N_2.[13] A large number of complex cobaltic selenates have been described.[14]

A good deal of work on ruthenium has been published. Ruthenium tetroxide is obtained in a state of purity by distilling at 40—50° in a current of air an acidified solution of a fused mass of ruthenium powder (1), potassium permanganate (2), and potassium hydroxide (20); it forms long, golden-yellow needles, readily soluble in water. The solution is unaffected by hydrofluoric acid, but readily oxidises the other halogen acids, liberating free halogen and

[12] J. G. F. Druce, *Chem. News*, 1925, **131**, 273; *A.*, ii, 1124; F. H. Loring and J. G. F. Druce, *ibid.*, 1925, **131**, 337; Dolejšek and Heyrovský, *Nature*, 1925, **116**, 782; see also *ibid.*, 1925, **117**, 16.

[13] F. W. Bergstrom, *J. Amer. Chem. Soc.*, 1924, **46**, 2631; *A.*, 1925, ii, 231.

[14] J. Meyer, G. Dirska, and F. Clemens, *Z. anorg. Chem.*, 1924, **139**, 333; *A.*, 1925, ii, 422.

yielding halogen derivatives of ter- and quadri-valent ruthenium.[15] A quantitative investigation of these reactions [16] affords strong evidence of the octavalency of ruthenium in the tetroxide. A detailed study has been made of the lower oxides of ruthenium: pure ruthenium dioxide may be prepared by heating ruthenium sesquichloride, Ru_2Cl_3, at 600—700° in oxygen and also by heating in a vacuum the tetrahydroxide obtained by the action of hydrogen peroxide on the trihydroxide.[17] Further investigation of tetrachlorodioxyruthenic acid, $H_2RuO_2Cl_4,3H_2O$,[18] has resulted in the isolation of a new ruthenium ammine, $Ru(NH_3)_3(H_2O)_2Cl_2$, ammonium and potassium hexachlororuthenates, $(Mt_4)_2RuCl_6,0{\cdot}5H_2O$ and K_2RuCl_6, and also a potassium pentachlororuthenite differing in many respects from those previously described.[19] This work must be considered in conjunction with an investigation directed especially to the chlororuthenites.[20]

Ruthenium pentafluoride has been prepared by direct union of its elements at 280° and forms a dark green, transparent mass, m. p. 101°, b. p. 270—275°, $d^{16{\cdot}5°}$ 2·963.[21]

Osmium tetroxide has been found to exist in two forms: the white needles produced when the vapour condenses in a cooled receiver melt at 39·5°, boil at 134°, and are readily soluble and reactive; when heated at 40°, they are converted into a yellow, sparingly soluble and non-reactive form, m. p. 41°, which may be reconverted into the white form by cooling in liquid air or by sublimation. Both forms had the calculated osmium content and liberated the calculated weight of iodine from potassium iodide.[22]

Iridium tetroxide has been obtained by heating the pure hydroxide in nitrogen at 350°,[23] and whilst attempts to prepare tetrahalides of iridium were unsuccessful, the monobromide, dibromide, tribromide, monoiodide, and di-iodide were obtained.[24] Lastly,

[15] F. Krauss and H. Kükenthal, *Z. anorg. Chem.*, 1924, **136**, 62; *A.*, 1925, ii, 480.

[16] O. Ruff and E. Vidic, *ibid.*, p. 49; *A.*, 1925, ii, 480.

[17] L. Wöhler, P. Balz, and L. Metz, *ibid.*, 1924, **139**, 205; *A.*, 1925, ii, 149.

[18] *Ann. Reports*, 1924, **21**, 54.

[19] Howe, *J. Amer. Chem. Soc.*, 1901, **23**, 775; *A.*, 1902, ii, 86.

[20] S. H. C. Briggs, *J.*, 1925, **127**, 1042; see also R. Charonnat, *Compt. rend.*, 1925, **180**, 1271; *A.*, ii, 586.

[21] O. Ruff and E. Vidic, *Z. anorg. Chem.*, 1925, **143**, 163; *A.*, ii, 443.

[22] F. Krauss and D. Wilken, *Z. anorg. Chem.*, 1925, **145**, 151; *A.*, ii, 894; compare H. von Wartenburg, *Annalen*, 1924, **440**, 97; 1925, **441**, 318; *A.*, ii, 231, 276.

[23] F. Krauss and H. Gerlach, *Z. anorg. Chem.*, 1925, **143**, 125; *A.*, ii, 424.

[24] *Idem, ibid.*, 1925, **147**, 265; *A.*, ii, 1089.

reference may be made to the isolation of a number of compounds of carbon monoxide with halogen compounds of iridium, osmium, rhodium, and ruthenium.[25]

H. V. A. Briscoe.

[25] W. Manchot and H. Gall, *Ber.*, 1925, **58**, [*B*], 232; W. Manchot and J. König, *ibid.*, 1924, **57**, [*B*], 2130; 1925, **58**, [*B*], 229, 2173; *A.*, ii, 232, 149, 232, 1193.

ORGANIC CHEMISTRY.

Part I.—Aliphatic Division.

The number of contributions in this section published during the year under review is again very large. The year has been marked by steady progress, with very definite achievements in certain groups, notably among the higher fatty acids and the complex carbohydrates. It has been found convenient to review the subject of optical activity every other year, so a detailed report will appear in the volume for 1926. Attention may, however, be directed in passing to a paper on the optical activity of the *n*-alkyl *p*-toluenesulphinates [1] and to another [2] dealing with the arrest of the mutarotation of tetramethyl glucose, each of which appears to open up a wide field.

Alcohols and their Derivatives.

Methyl alcohol can be obtained in a highly purified condition [3] by fractionating through a Hempel column of an effective length of 1·3 metres, and refluxing with aluminium amalgam. To remove ammonia, it is then refluxed under a column packed with dehydrated copper sulphate. By this means methyl alcohol having a conductivity of 0·04 reciprocal megohm has been prepared. To test for the presence of impurities in methyl alcohol, a reagent consisting of a concentrated solution of mercuric cyanide in 6*N*-sodium hydroxide is suggested. A white precipitate indicates the presence of a ketone; if the precipitate darkens on keeping, an aldehyde also is present. The reagent will show the presence of 0·002% of acetone or 0·004% of formaldehyde if either is present alone. The most sensitive test for water is the variation observed in the electrical conductivity of a dilute solution of hydrogen chloride in the alcohol. Ethyl alcohol can be dehydrated by successive distillation with calcium chloride [4] until a concentration of 98% is attained. Cetyl alcohol in a nearly pure condition can be easily and quickly prepared [5] by hydrolysis of spermaceti in aqueous-alcoholic potassium

[1] H. Phillips, *J.*, 1925, **127**, 2552. [2] T. M. Lowry, *ibid.*, p. 1385.

[3] H. Hartley and H. R. Raikes, *ibid.*, p. 524.

[4] J. J. Sudborough and P. R. Ayyar, *J. Indian Inst. Sci.*, 1925, **8A**, 49; *A.*, i, 1125.

[5] M. A. Youtz, *J. Amer. Chem. Soc.*, 1925, **47**, 2252; *A.*, i, 1125.

hydroxide solution followed by extraction, under specified conditions, with light petroleum. It is purified by conversion into the acetate, which may be distilled under reduced pressure.

The use of magnesium alkyloxides in the synthesis of alcohols has been examined.[6] These are prepared by passing the vapours of the alcohols over magnesium at 270—280°. In 1 hour the reaction is complete and on raising the temperature to 400—410° for 2 to 3 hours more, the alcohol vapour, by interaction with the ethoxide, produces the higher alcohol. Ethyl alcohol is thus found to give butyl alcohol in 12—18% yield, whilst propyl alcohol gives dipropyl alcohol (β-methylpentanol) in 30% yield. Primary acetylenic alcohols, $CR{:}C{\cdot}CH_2{\cdot}OH$, are obtained readily [7] by the action of gaseous formaldehyde on the magnesium bromide derivative of the corresponding acetylene. Phenylpropiolic alcohol, for example, may be prepared in this way and it is noteworthy that all these acetylenic alcohols have a fragrant odour.

A study of the production of glycerol by the fermentation of sugar [8] shows that the hydrogen-ion concentration of the solution is the deciding factor. The addition of sodium hydrogen sulphite during the fermentation, in quantities sufficient to maintain the proportion of free sulphite constant, has an important effect on the production of glycerol, the amount of which, under such conditions, approaches 40% of the sugar converted. The best method for the preparation of the simple methylalkylglycerols would appear to be [9] the treatment of the dibromohydrin with potassium acetate followed by hydrolysis of the diacetate with methyl alcohol. The yield of, *e.g.*, methyl-*n*-propylglycerol by this method is about 40% compared with less than 20% by other processes.

A number of new asymmetric tertiary alcohols of high molecular weight have been prepared from methyl nonyl ketone by the Grignard reaction.[10] On dehydration of these alcohols with acetic anhydride or sulphuric acid, water is lost and an ethylenic hydrocarbon results. It is found that in most cases the elements of water are eliminated by reaction between the hydroxyl group and a hydrogen atom from the largest alkyl group present, *e.g.*, methylethylnonylcarbinol yields γ-methyl-Δ$^{\gamma}$-dodecene.

It was formerly supposed that the gossypyl alcohol obtained from cotton wax was present in three varieties. A closer examination [11] shows that this is not the case and that the alcohols actually present

[6] A. Terentier, *Bull. Soc. chim.*, 1924, [iv], **35**, 1145.
[7] H. H. Guest, *J. Amer. Chem. Soc.*, 1925, **47**, 860; *A.*, i, 627.
[8] Y. Tomoda, *J. Fac. Eng. Tokyo*, 1924, **15**, 193; *A.*, 1925, i, 227.
[9] R. Delaby and G. Morel, *Compt. rend.*, 1925, **180**, 1408; *A.*, i, 773.
[10] H. Thoms and B. Ambrus, *Arch. Pharm.*, 1925, **263**, 241; *A.*, i, 789.
[11] *J. Text. Inst.*, 1924, **15**, *T*, 337; *A.*, 1925, i, 879.

in the wax of American cotton are (*a*) montanyl alcohol, $C_{28}H_{58}O$, (*b*) gossypyl alcohol, $C_{30}H_{62}O$, and, in smaller quantity, alcohols, $C_{32}H_{66}O$ and $C_{34}H_{70}O$, together with a glycol, $C_{29}H_{60}O_2$, which is probably a mixture. The wax-ester compounds isolated, included gossypyl carnaubate, gossypyl gossypate, and montanyl montanate.

The catalytic power of salts in promoting acetal formation appears to be connected with their capacity to form alcoholates.[12] All the known catalysts for acetal formation give acid solutions with water, but that hydrogen ion is the catalyst is disproved by the fact that calcium chloride, *e.g.*, is more efficient than zinc chloride or ferric chloride. The velocity of acetal formation with hydrogen chloride as catalyst has been investigated in thirty-two cases. The velocity is least with methyl alcohol, *n*-butyl alcohol being next, but secondary, and especially tertiary, alcohols react much more rapidly. The highest reaction affinities were observed when four carbon atoms were situated on either the alcohol or the aldehyde side of the acetal, and the lowest when the aldehyde had a double bond in the $\beta\gamma$-position, as in furfuraldehyde and cinnamaldehyde. Butaldehyde had the slowest reaction speed, whilst furfuraldehyde and heptaldehyde, at the other end of the series, reacted several hundred times more rapidly. The method suggested by Ghysels [13] for the preparation of the formals of primary alcohols has been applied [14] to the preparation of acetals $CH_3{\cdot}CH(OR)_2$. The alcohol mixed with paraldehyde is heated with 1 to 2% of *p*-toluenesulphonic acid. The isolation of the product is complicated by the formation of binary azeotropic mixtures between the alcohol and the acetal. The acetal, however, can be separated from these by the addition of carbon disulphide, which forms, in most cases, a further azeotropic mixture with the acetal. The yields amount to some 65%.

Ethyl acetate of high purity is obtained [15] by heating alcohol with glacial acetic acid and 0·1% of sulphuric acid for 10 minutes. The best yield of ethyl acetoacetate was obtained by the action of clean sodium on a mixture of pure ethyl acetate containing 5% of absolute alcohol. A stable solution of ethyl hypochlorite can be obtained [16] by shaking hypochlorous acid with carbon tetrachloride containing 2% of ethyl alcohol. The ester formed remains dissolved in the carbon tetrachloride. The solution can be used at a low temperature to study the action of ethyl hypochlorite on organic

[12] E. W. Adams and H. Adkins, *J. Amer. Chem. Soc.*, 1925, **47**, 1358, 1368; *A.*, i, 784, 785.

[13] *A.*, 1924, i, 490.

[14] J. Bédowé, *Bull. Soc. chim. Belg.*, 1925, **34**, 41.

[15] K. G. Roberts, *J. Soc. Chem. Ind.*, 1924, **43**, 295T.

[16] M. C. Taylor, R. B. McMullin, and C. A. Gammal, *J. Amer. Chem. Soc.*, 1925, **47**, 395; *A.*, i, 501.

compounds.[17] This appears to consist generally in the hydrolysis of the ester to ethyl alcohol and hypochlorous acid with subsequent addition of the latter at an aliphatic double bond. Amylene, for example, gives amylenechlorohydrin. On the other hand, with 1 : 4-dihydronaphthalene direct addition of the ester occurs, 3-chloro-2-ethoxy-1 : 2 : 3 : 4-tetrahydronaphthalene being the chief product. Ethyl hypochlorite was also found very suitable for the chlorination of primary and secondary amines, ethylamine, for example, yielding ethyldichloroamine.

In continuation of his studies on keto-enolic desmotropy, H. P. Kaufmann [18] shows that the capacity to add bromine is not a characteristic property of all enols, as it may be suppressed by steric influences, or by the presence of negative groups; and further, that some enols do not give a characteristic coloration with ferric chloride. The discrepancies obtained in the determination of enol in ethyl diacetylsuccinate as well as in γ-methylacetylacetone are shown to be due to water in the iodide solution employed.[19] With alcoholic sodium iodide solution, the difficulties disappear.

A chelate ring structure for the enolic form of acetoacetic ester is proposed [20] in conformity with evidence already adduced in the case of ortho-substituted phenols. The argument is based upon the statement that if the enol is chelate it will not be associated and its b. p. will be lower than that of the ketone, and its solubility will be less in water and more in non-polar solvents. For the enol of ethyl acetoacetate, the requisite data are available from the work of Meyer and Schöller.[21] These results show that the solubilities and boiling point are in agreement with the above hypothesis of a ring structure and the consequent absence of a hydroxyl group in the enol, for which the following formula is suggested :

Aldehydes and Ketones.

A new method [22] for the synthesis of aldehydes consists in the conversion of a nitrile, through the imino-chloride, into an aldehyde containing the same number of carbon atoms. Anhydrous stannous chloride, dissolved in ether saturated with hydrogen chloride, is the most satisfactory reducing agent. The reactions which occur are as follows :

[17] S. Goldschmidt, R. Endres, and R. Dirsch, *Ber.*, 1925, **58**, [*B*], 572; *A.*, i. 502.
[18] H. P. Kaufmann and E. Richter, *ibid.*, p. 216; *A.*, i, 231.
[19] H. P. Kaufmann and J. Liepe, *ibid.*, p. 1560; *A.*, i, 1241.
[20] N. V. Sidgwick, *J.*, 1925, **127**, 907.
[21] *Ber.*, 1920, **53**, 1410; *A.*, 1920, i, 707.
[22] H. Stephen, *J.*, 1925, **127**, 1874.

$$R{\cdot}CN + HCl \longrightarrow R{\cdot}CCl{:}NH; \quad R{\cdot}CCl{:}NH + SnCl_2 + 2HCl \longrightarrow R{\cdot}CH{:}NH,HCl + SnCl_4.$$

As examples of the utility of the method, *n*-octaldehyde, myristaldehyde, and stearaldehyde, besides a number of aromatic aldehydes, have been prepared, the yields in many cases being almost quantitative.

The term ketocyclic desmotropy has been applied [23] to the desmotropy existing between an open and a cyclic form such as that assumed in the case of the sugars and established for γ- and δ-hydroxyaldehydes. Further work has shown that hydroxyaldehydes in which the hydroxy- and the aldehydo-groups are far apart are also capable of existing in cyclic forms. Thus ι-hydroxynonaldehyde, by the action of methyl-alcoholic hydrogen chloride, is converted into the methyl-semi-acetal $\underset{\llcorner\!\!-\!\!-O-\!\!-\!\!-\lrcorner}{CH_2{\cdot}[CH_2]_7{\cdot}CH{\cdot}OMe}$, a ten-membered ring being thus formed. The general reaction may be represented as

$$O{:}\overset{|}{C}- \cdots -\overset{|}{\underset{OH}{C}} \longrightarrow HO-\overset{|}{C}- \cdots -\overset{|}{C}-$$

and either an acyl or an alkyl group may be substituted for the hydrogen atom.[24] It is proposed to designate these *cyclo*-forms of carbonyl compounds by the general term "lactoles," aldo-lactoles and keto-lactoles being derived from hydroxy-aldehydes and hydroxy-ketones, respectively. The *O*-alkyl derivatives of lactoles are called lactolides to express their relation to the glucosides. The following examples illustrate these new collective terms: $\underset{\llcorner\!\!-O-\!\!-\lrcorner}{HO{\cdot}CH{\cdot}[CH_2]_2{\cdot}CHMe}$, γ-valerolactole [25]; $\underset{\llcorner\!\!-O-\!\!-\lrcorner}{MeO{\cdot}CH{\cdot}[CH_2]_2{\cdot}CHMe}$, γ-valeromethyl-lactolide; $\underset{\llcorner\!\!-O-\!\!-\lrcorner}{AcO{\cdot}CH{\cdot}[CH_2]_2{\cdot}CHMe}$, γ-valerolactole acetate. The simpler sugars also could be included in this nomenclature.

A method for the reduction of aldehydes and certain ketones to alcohols has been worked out by H. Meerwein and R. Schmidt,[26] who have studied the conditions necessary for the action of metal alkyloxides on aldehydes. When an aldehyde is treated with aluminium ethoxide in absolute alcoholic solution the following reactions appear to take place (al = 1/3Al): $R{\cdot}CHO + alOEt \rightleftharpoons R{\cdot}CH(Oal){\cdot}OEt \longrightarrow R{\cdot}CH_2{\cdot}Oal + O{:}CHMe$. The second stage recalls the decomposition of benzaldehydeacetal into acetaldehyde and benzyl ethyl ether and the formation of aldehydes and hydro-

[23] B. Helferich and H. Köster, *Ber.*, 1923, **56**, [*B*], 2088; *A.*, 1923, i, 1177.
[24] B. Helferich and F. A. Fries, *ibid.*, 1925, **58**, [*B*], 1246; *A.*, i, 1039.
[25] B. Helferich, *ibid.*, 1919, **52**, 1123.
[26] *Annalen*, 1925, **444**, 221; *A.*, i, 1239.

carbons from ethers. By the use of aluminium ethoxide, yields of 80—90% of the amount of alcohol theoretically possible were obtained in the course of a few days at the ordinary temperature. The process was successful also with α-unsaturated aldehydes and with those containing nitro- or halogen radicals, but not with amino- or hydroxy-aldehydes. Those ketones which readily form alkyloxides, *e.g.*, α-diketones, are the only ones easily reduced by this method. It is interesting from a biochemical point of view to note that those aldehydes and ketones which readily reduce with aluminium ethoxide are easily reduced by phytochemical processes and *vice versa*. The alkyloxides of calcium and magnesium are without reducing action, as is also the less basic calcium ethoxychloride; on the other hand, magnesium ethoxychloride is as active as aluminium ethoxide. The paper contains an account of special methods for the preparation of these reducing agents.

An analogous explanation of the action of aluminium ethoxide is suggested by A. Verley,[27] who agrees that the Tischtschenko [28] reaction, $2R{\cdot}CHO = R{\cdot}CO{\cdot}O{\cdot}CH_2R$, is quite secondary. He suggests that the cycle comprises four stages, of which the first results in the formation of a hemi-acetal (I), which passes to the compound (II). This then dissociates, as shown, and the compound (III) by interaction with alcohol gives $CH_2R{\cdot}OH$. A similar interchange of functional groups takes place with ketones and the aluminium alkyloxides.

$$\underset{\text{(I.)}}{Al(OEt)_2{\cdot}O{\cdot}CHR{\cdot}O{\cdot}CH_2Me} \longrightarrow \underset{\text{(II.)}}{Al(OEt)_2{\cdot}O{\cdot}CHMe{\cdot}O{\cdot}CH_2R} \longrightarrow Me{\cdot}CHO + \underset{\text{(III.)}}{CH_2R{\cdot}O{\cdot}Al(OEt)_2}$$

The sodium alkyloxides, however, react more rapidly. Methyl nonyl ketone, for example, with sodium *iso*propoxide gives a quantitative yield of undecan-β-ol and acetone.

An examination [29] of the utility of aluminium ethoxide as a reagent for the condensation of aldehydes to esters shows that in its presence acetaldehyde and heptaldehyde condense at about the same rate and faster than benzaldehyde, which, itself, is faster than furfuraldehyde. Aluminium ethoxide reacts with certain metallic chlorides, forming compounds of the type $AlCl_3{,}3Al(OEt)_3$ in the case of aluminium and ferric chlorides and $HgCl_2{,}2Al(OEt)_3$ in the case of mercuric and zinc chlorides. These compounds are much more active in ester

[27] *Bull. Soc. chim.*, 1925, [iv], **37**, 537, 871; *A.*, i, 783, 1034.
[28] *A.*, 1907, i, 282.
[29] W. C. Child and H. Adkins, *J. Amer. Chem. Soc.*, 1925, **47**, 798; *A.*, i, 632.

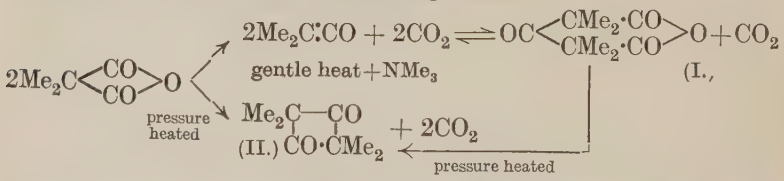
condensation than the aluminium ethoxide itself. A comparison of analogous catalysts in the case of the condensation of acetaldehyde to ethyl acetate showed that the catalytic activity increased in order from titanium ethoxide to aluminium ethoxide to aluminium *iso*propoxide and aluminium butoxide, the efficiencies of the last two being approximately equal.

A synthesis of α-hydroxyketones [30] is based upon the observation that catalytic reduction converts the grouping $-CCl(NO_2)-$ into $-CO-$; thus $>CCl\cdot NO_2+6H=:CO+NH_4Cl+H_2O$. Using hydrogen with palladised barium sulphate as catalyst, γ-chloro-γ-nitropentane-βδ-diol was converted into pentane-β-ol-γ-one and β-chloro-β-nitrobutane-αγ-diol into butan-β-ol-β-one, which latter appears to exist in the cyclic form $CH_2Me\cdot C(OH)\cdot CH_2$ (with the O bridging the OH and the CH$_2$). A study [31] of the Claisen condensation shows that in a number of cases the condensation between ketones and esters is the normal one at low temperatures, but at higher temperatures alcoholysis takes place with decomposition of the αγ-diketone. Diethyl ketone, for example, reacts normally with ethyl acetate at room temperature in the presence of sodium to give γ-methylhexa-βδ-dione, MeCO·CHMe·COEt, but on warming towards the end of the reaction, hexa-βδ-dione is formed. The explanation suggested is that the excess of ethyl acetate undergoes condensation with methyl ethyl ketone, which is produced by the decomposition of a sodium derivative of γ-methylhexa-βδ-dione according to the following scheme: $(MeCO\cdot CMe\cdot COEt)Na+2EtOH = NaOEt+C_2H_5\cdot CO_2Et+Me\cdot CO\cdot Et$ (or perhaps $CH_3\cdot CO_2Et+Et\cdot CO\cdot Et$). A large number of similar reactions were observed. Calcium hydride,[32] when used as a reagent with ketones, is found to resemble calcium carbide in that it brings about condensation only with those compounds containing the group $CO\cdot CH_3$. On diethyl ketone, for example, it has no appreciable action. With methyl ethyl ketone, it gives one only of the possible isomeric homomesitones, CMeEt:CH·COEt, resembling, in this respect, similar condensing agents.

The optimum conditions for the preparation of keten from acetone are given by C. D. Hurd and W. H. Tallyn [33] as follows: the acetone must be passed through a "pyrex" tube kept at 700° at the rate of 5 c.c. per minute. In this way, the maximum yield of some 40% is obtained. Acetylacetone also undergoes pyrogenic decomposition into keten, the maximum yield of 16·7% being obtained at about 630°.

[30] E. Schmidt and A. Ascherl, *Ber.*, 1925, **58**, [*B*], 356; *A.*, i, 364.
[31] G. T. Morgan, H. D. K. Drew, and C. R. Porter, *ibid.*, p. 333; *A.*, i, 363.
[32] C. Porlezza and U. Gatti, *Gazzetta*, 1925, **55**, 224; *A.*, i, 788.
[33] *J. Amer. Chem. Soc.*, 1925, **47**, 1427, 1779; *A.*, i, 785, 885.

Further contributions to the chemistry of the ketens are contributed by H. Staudinger and his co-workers. It was known that dimethylketen, in an atmosphere of nitrogen or hydrogen and in the presence of a trace of trimethylamine, gave a colloidal polymerisation product. It was discovered [34] that in an atmosphere of carbon dioxide at a low temperature addition products are formed of the nature $2Di,1CO_2$; $3Di,2CO_2$; $4Di,3CO_2$. The first of these products is a crystalline substance which was shown to be tetramethylacetonedicarboxylic anhydride (β-keto-ααγγ-tetramethylglutaric anhydride) (I), since on hydrolysis it yields dimethylmalonic and *iso*butyric acids. This compound was also obtained by the decomposition of dimethylmalonic anhydride in a sealed tube at 100° in the presence of trimethylamine. If the catalyst were omitted, however, 1 : 1 : 3 : 3-tetramethyl*cyclo*butane-2 : 4-dione (II) was formed in quantitative yield. The formation of these substances is shown in the following scheme :



Analogous products were obtained by the interaction of carbon disulphide, and various carbimides, with dimethylketen at 80° in the presence of trimethylamine, although these differed in being highly polymerised. Amorphous polydimethylketens of high molecular weight were obtained by keeping dimethylketen, containing a trace of trimethylamine, at −80°. The polymerides revert to the mother-substance when heated at 100—200°. A crystalline polyketen, $(C_2H_2O)_4$, has also been prepared which seems to form a link between the colloidal polydimethylketens and the crystalline *cyclo*butanedione compounds. In order to explain the differences observed in the physical properties of the crystalline and the colloidal additive and polymerisation products of dimethylketen, it is supposed that the crystalline derivatives, *e.g.*, β-keto-ααγγ-tetramethylglutaric anhydride (I), contain closed rings, whilst in the colloidal derivatives, ring closure, for various reasons, is impossible and these compounds consist of long chains of units of the type . . $(CO{\cdot}CMe_2{\cdot}CO{\cdot}NR{\cdot}CO{\cdot}CMe_2{\cdot}CO{\cdot}NR{\cdot}CO{\cdot}CMe_2)_x$., for example.

Acids.

The question of the formation of fatty acids from paraffins has been studied by Marcusson,[35] who submitted ozokerite to the action

[34] H. Staudinger, *Helv. Chim. Acta*, 1925, **8**, 306; *A.*, i, 786.
[35] *Chem.-Ztg.*, 1925, **49**, 166; *A.*, i, 349.

of oxygen in the presence of manganese dioxide and fuller's earth. At 125°, the action was slow, but at 150° an acid value of 39 was attained after 90 hours. The liquid acid fraction consisted of a mixture of polymerised unsaturated fatty acids. The solid acids melted at 60—62° with a molecular weight of 384. Convenient methods for the preparation of acids are given by various authors. S. G. Powell [36] finds that β-chloropropionic acid can be obtained in a yield of more than 50% by adding trimethylenechlorohydrin to concentrated nitric acid. By the action of hydrogen chloride gas on aniline trichloroacetate in the presence of copper, H. W. Doughty and A. P. Black [37] have obtained a 75% yield of dichloroacetic acid.

The optimum conditions for the preparation of *n*-valeric acid from magnesium butyl bromide and carbon dioxide have been examined.[38] A low temperature between 0° and −20° is found essential [39] in order to obtain a yield of the order of 80—86%. At higher temperatures, tributylcarbinol is produced, the yield of *n*-valeric acid falling to below 10% of the theoretical.

J. W. E. Glattfield and L. P. Shearman,[40] in continuation of their researches on "saccharinic acids," describe the preparation of *dl*-αβ-dihydroxy*iso*butyric acid. The saccharinic acids are defined as those acids which would result from the hydroxyaldehydes of the formula $C_nH_{2n}O_2$ which have one hydroxyl group attached to each carbon atom (except the aldehyde carbon atom), if the oxidation took place at the expense of one of the ⋮C·OH groups—this group itself becoming reduced to a ⋮CH group. Thus αβ-dihydroxy*iso*-butyric acid is regarded as a saccharinic acid derived from tri-hydroxy*iso*butaldehyde. The acid is obtained by the action of silver oxide on β-chloro-α-hydroxy*iso*butyric acid, the yield being 32% as compared with 10—15% by other methods.

Simpler Unsaturated Fatty Acids.—Acetylenic compounds, on hydrogenation at the ordinary temperature in the presence of colloidal palladium,[41] or of nickel,[42] are converted almost completely into *cis*-ethylenic compounds. Among the acetylenic acids investigated, phenylpropiolic acid is converted entirely into *iso*-cinnamic acid; tetrolic acid into *iso*crotonic acid, and acetylene-dicarboxylic acid gives solely maleic acid. The general conclusion is drawn that acids of the type CR⋮C·CO_2H react similarly on

[36] *J. Amer. Chem. Soc.*, 1924, **46**, 2879; *A.*, 1925, i, 228.
[37] *Ibid.*, 1925, **47**, 1091; *A.*, i, 628.
[38] H. Gilman and H. H. Parker, *ibid.*, 1924, **46**, 2816; *A.*, 1925, i, 228.
[39] D. Ivanov, *Bull. Soc. chim.*, 1925, [iv], **37**, 287; *A.*, i, 503.
[40] *J. Amer. Chem. Soc.*, 1925, **47**, 1742; *A.*, i, 881; compare *A.*, 1921, i, 7; 1922, i, 318.
[41] M. Bourguel, *Compt. rend.*, 1925, **180**, 1753; *A.*, i, 883.
[42] A. González, *Anal. Fís. Quím.*, 1925, **23**, 100; *A.*, i, 629.

hydrogenation with a metallic catalyst whether R is an aryl or an alkyl group.

Considerable attention has been devoted to the problems associated with fumaric and maleic acids. Maleic anhydride has been obtained to the extent of 99% of the theoretical amount by distilling maleic acid with 70% of its weight of phosphoric oxide at 100° under reduced pressure.[43] The almost quantitative conversion of fumaric or maleic acid into racemic or *meso*tartaric acid has also been accomplished by N. A. Milas and E. M. Terry,[44] using sodium chlorate as the oxidising agent in the presence of osmium tetroxide.

The question of the transmutation of maleic acid into fumaric acid has been examined by E. M. Terry and L. Eichelberger,[45] who consider that the reaction is due to the formation, in the first instance, of an additive complex, each carboxyl group of the acid adding one molecule of the catalyst. The effect of this addition is to "activate" the complex at the ·C:C· linking, the active form being depicted as an electromeride, $\cdot\overset{+}{C}\cdot\overset{-}{C}\cdot$, which thus becomes free to assume the *trans*-configuration. The theory is based on measurements of the velocity of conversion of maleic acid in aqueous solution in the presence of hydrochloric acid or of potassium thiocyanate. No by-products were formed and the velocity was found to be proportional to the concentration of the catalyst and to the second power of the initial concentration of the maleic acid. It is thought that the "activation" stage is comparatively slow, and that it is the velocity of this that is actually measured. The action of bromine on these acids in aqueous solution, which was found to result in the formation of 78% of dibromosuccinate and 10% of *iso*dibromosuccinate, is similarly explained. H. Meerwein and J. Weber[46] also consider that the capacity of catalysts to cause the transformation of these stereoisomeric ethylenic compounds depends on their power of activating the double bond. All substances, therefore, which are capable of addition at the double bond should catalytically accelerate the transformation. In support of this view, it is shown that metallic potassium, which is known to have the power of addition at the ethylenic linking, converts methyl maleate into methyl fumarate in the presence of dry ether.

Some interesting observations on inversion phenomena, coupled with a discussion on the bearing of the results on the stereochemistry

[43] E. M. Terry and L. Eichelberger, *J. Amer. Chem. Soc.*, 1925, **47**, 1067; *A.*, i, 631.

[44] *Ibid.*, p. 1412; *A.*, i, 780.

[45] *Ibid.*, pp. 1402, 1067; *A.*, i, 780, 631.

[46] *Ber.*, 1925, **58**, [*B*], 1266; *A.*, i, 1038.

of the αβ-diols, sugars, etc., is contributed by R. Kuhn and F. Ebel.[47] When hypochlorous acid reacts with maleic acid the sole product is a chloromalic acid I, m. p. 145°, but with fumaric acid the reaction is not homogeneous, a chloromalic acid II, m. p. 153·5°, being one only of the products. These acids differ greatly in the ease of replacement of halogen by the hydroxy-group, the half-periods under identical conditions for chloromalic acids I and II being 18 and 200,000 minutes, respectively.

Loss of hydrogen chloride converts chloromalic acid I into a fumarylglycidic acid, which was resolved into its optical antipodes and is therefore regarded as *trans*-oxidoethylene-αβ-dicarboxylic acid (III). Chloromalic acid II yields a *cis*-oxidoethylene-αβ-dicarboxylic acid (IV), which resisted all attempts at resolution. The *trans*-acid (III) on treatment with boiling water gave a mixture of *r*-tartaric acid (37%) and *meso*tartaric acid (63%), whilst the *cis*-acid (IV) gave only *r*-tartaric acid, the homogeneous reaction in this case being comparable with that between hypochlorous acid and maleic acid. It thus appears that *cis*-compounds, in additive reactions, yield one derivative only, while *trans*-compounds give a mixed product. These and other observations are included in the following scheme,

trans-oxidoethylene-αβ-dicarboxylic acid (III) $\xrightarrow{+H_2O}$ *r*- and *meso*-tartaric acids

$\uparrow -HCl$

Chloromalic acid I $\xrightarrow{\text{action of } H_2O}$ *r*- and *meso*-tartaric acids

Chloromalic acid II $\xrightarrow{\text{action of } H_2O}$ *meso*-tartaric acid alone

$\downarrow -HCl$

cis-oxidoethylene-αβ-dicarboxylic acid (IV) $\xrightarrow{+H_2O}$ *r*-tartaric acid alone

which shows that it is possible to convert the *cis*-acid (IV) either directly into *r*-tartaric acid or indirectly, through chloromalic acid II, into *meso*tartaric acid. The claim that the conversion of *cis*-oxidoethylenedicarboxylic acid into *r*-tartaric acid is the first recorded instance of quantitative transfission of a ring system is disputed by J. Böeseken.[48]

Further light has been thrown on the double linking in such geometrical isomerides as fumaric and maleic acids by the application of the concept of the parachor.[49] This quantity, which involves surface tension and density, can be expressed [50] as a simple

[47] *Ber.*, 1925, **58**, [*B*], 919, 1447; *A.*, i, 780, 1237.
[48] *Ibid.*, 1470; *A.*, i, 1237.
[49] S. Sudgen and H. Whittaker, *J.*, 1925, **127**, 1868.
[50] *Ann. Report*, 1924, p. 8.

additive function of certain atomic and structural constants. If the values of these constants are known, the theoretical parachor can be calculated. It has further been shown [51] that the parachor enables a distinction to be drawn between the two types of double bonds predicted by the octet theory of valency, *viz.*, the ordinary non-polar double bond, which consists of two co-valencies, and the semipolar double bond, made up of one co-valency and one electro-valency. The presence of one of the former is found to add 23·2 units to the parachor, whilst the latter lowers the parachor by 1·6 units. Langmuir has assumed that carbon–carbon double bonds are non-polar, and Sugden [52] has suggested that there must be free rotation round a semi-polar double bond, so that it would be expected that unsaturated compounds exhibiting geometrical isomerism would have a linking of the non-polar type. Measurements of the parachors of *cis-* and *trans*-unsaturated esters are now recorded, and in every case the experimental value agrees closely with the theoretical value, calculated on the assumption that a non-polar double bond is present. The investigation included the esters of fumaric acid and maleic acid, mesaconic and citraconic acids, and cinnamic and *allo*cinnamic acids.

It was suggested in a previous Report [53] that an *X*-ray study of fumaric and maleic acids might afford valuable information regarding the isomerism exhibited by this series of acids. The preliminary results of such an investigation are now reported.[54]

Higher Fatty Acids and their Derivatives.—A very large amount of work has been carried out in this field during the year. The separation of the fatty acid components of the natural oils and fats has been studied by various authors. The fractional distillation of the methyl or ethyl esters of the separated fatty acids has been shown [55] to be a very satisfactory method for the separation of the mixed fatty acids, provided that in certain cases the solid and liquid acids are separately esterified and other precautions taken. These esters form the basis of a new procedure,[56] by which the position of the ethylenic linking in acids of the oleic series can be determined. Methods previously employed are complicated, and open to the objection that migration of the ethylenic linking is not excluded, whilst the products obtained are complex mixtures from which it is difficult to deduce a structural formula. It was found that

[51] Sudgen, Reed, and Wilkins, *J.*, 1925, **127**, 1525.
[52] *J.*, 1923, **123**, 1864.
[53] *Ann. Report*, 1923, p. 69.
[54] K. Yardley, *J.*, 1925, **127**, 2207.
[55] E. F. Armstrong, J. Allan, and C. W. Moore, *J. Soc. Chem. Ind.*, 1925, **44**, 63T; *A.*, i, 353.
[56] E. F. Armstrong and T. P. Hilditch, *ibid.*, p. 43T; *A.*, i, 355.

oxidation of the methyl or ethyl esters with permanganate in hot acetone or acetic acid solution leads definitely to the production of the monobasic and dibasic acids corresponding to the position of the ethylenic linking, in very high yield, *viz.*, about 80% of the theoretical yield of the dibasic, and rather less of the monobasic, acid. Ethyl oleate gave azelaic acid amounting to 95% and nonoic acid 59% of the theoretical.

Extending these methods to the constituents of whale oil from South Georgia, the authors show[57] that the unsaturated acids present include myristolenic acids C_{14} (1—1·5%), chiefly Δ^{4}-tetradecenoic acid mixed with a small quantity of the Δ^{7}- or Δ^{6}-acid; palmitolenic acid C_{16} (15%), identified as entirely Δ^{4}-hexadecenoic acid; an oleic acid C_{18}, Δ^{4}-octadecenoic acid, with a very small proportion of the Δ^{5}-derivative. These are of the semi-drying or moderately unsaturated type. In addition, however, some acids were isolated which appear to be in a class apart. They fall into the C_{20} and C_{22} series, and are so highly unsaturated that the average total unsaturation, expressed in terms of ethylenic linking, amounts to four or five of the latter. In these acids, as in the others isolated, no double bonds appear nearer the carboxyl group than the $\Delta^{9:10}$-position, an observation which may possess some biochemical significance.

Chinese wood oil is found to contain[58] up to 90% of the glyceride of α-elæostearic acid. This, $CH_3{\cdot}[CH_2]_3{\cdot}[CH{:}CH]_3{\cdot}[CH_2]_7{\cdot}CO_2H$, was converted under the action of ultra-violet rays into the β-derivative. Elæostearic acid has been considered an isomeride of linoleic acid, but a study of the molecular refractivities of the α- and β-acids, their glycerides and the α-ethyl ester shows that in all probability three conjugated double bonds are present. The formula given above is therefore suggested for these acids, and the high degree of unsaturation has been confirmed by hydrogenation in the presence of a nickel catalyst.

The glycerides of cacao fat have been shown[59] to consist of 55% of glyceryl α-palmitate βγ-dioleate, 20% of glyceryl β-palmitate αγ-distearate, 25% of glyceryl αβ-distearate γ-oleate with small quantities of glyceryl β-palmitate αγ-distearate and tristearin. G. T. Morgan and A. R. Bowen[60] also find that no higher acid

[57] E. F. Armstrodg and T. P. Hilditch, *J. Soc. Chem., Ind.*, 1925, **44**, p. 180T; *A.*, i, 778.

[58] J. Böeseken and (Mlle.) H. J. Ravenswaay, *Rec. trav. chim.*, 1925, **44** 241; *A.*, i, 507. See also *Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 386; *A.*, i, 1129.

[59] K. Amberger and J. Bauch, *Z. Unters. Nahr. Genussm.*, 1924, **48**, 371; *A.*, 1925, i, 114.

[60] *J. Soc. Chem. Ind.*, 1924, **43**, 346; *A.*, 1925, i, 114.

than stearic acid is contained in cacao fat, so that it is useless as a source of eicosanoic acid. They note that stearic and eicosanoic acids form a compound $C_{18}H_{36}O_2$,$C_{20}H_{40}O_2$ and that a mixture containing 50% of each is not separable by fractional crystallisation. The occurrence of a highly unsaturated acid, $C_{22}H_{36}O_2$, in various algæ has been recorded.[61] The acid gives a bromo-derivative, $C_{22}H_{36}O_2Br_8$, and on reduction yields behenic acid.

Successful attempts to develop methods which could be applied to the synthesis of the naturally occurring unsaturated fatty acids are reported by G. M. and R. Robinson.[62] Concentrating first on the synthesis of oleic acid, it was found that this acid had previously been obtained from 10-ketostearic acid, $CH_3{\cdot}[CH_2]_7{\cdot}CO{\cdot}[CH_2]_8{\cdot}CO_2H$, by reduction of the CO group followed by conversion to 10-iodostearic acid and treatment of this with alcoholic potassium hydroxide. The synthesis of 10-ketostearic acid was achieved by condensing ethyl sodio-2-acetylnonoate and 9-carbethoxynonyl chloride. The resulting ester, $CH_3{\cdot}[CH_2]_6{\cdot}CAc(CO_2Et){\cdot}CO{\cdot}[CH_2]_8{\cdot}CO_2Et$, on hydrolysis, yielded 10-ketostearic acid (m. p. 83°), which was converted, by the methods given above, into oleic acid identical with a pure specimen from olive oil supplied by A. Lapworth, who [63] has made a careful study of the isolation of pure oleic acid and the properties of its salts. The synthesis proves that the double bond in oleic acid is in the $\Delta^{9:10}$ or $\Delta^{10:11}$ position. To eliminate the latter alternative, attempts are in progress to synthesise stearolic acid, since this can be reduced by zinc and hydrochloric acid, in the presence of titanous chloride, to oleic acid, a reaction which indicates that oleic acid possesses the *cis*-configuration. The method of synthesis was also successfully employed in the case of lactarinic acid, which was originally isolated by Bougault and Chavaux [64] from various species of fungi and shown by them to be 6-ketostearic acid. The synthesis has now been accomplished by condensation of ethyl 2-acetyl-*n*-tridecoate and 5-carbethoxyvaleryl chloride, which gives the ester $CH_3{\cdot}[CH_2]_{10}{\cdot}CAc(CO_2Et){\cdot}CO{\cdot}[CH_2]_4{\cdot}CO_2Et$, from which, by graduated hydrolysis, lactarinic acid, $CH_3{\cdot}[CH_2]_{11}{\cdot}CO{\cdot}[CH_2]_4{\cdot}CO_2H$, was obtained identical with the natural product. 4-Ketopalmitic acid, $C_{16}H_{30}O_3$, also was prepared. Further development of these methods will be awaited with interest.

This work has led to an accurate estimation of the higher saturated acids in specimens of oleic acid.[65]

[61] M. Tsujimoto, *Chem. Umschau*, 1925, **32**, 125; *A.*, i, 778.
[62] *J.*, 1925, **127**, 175.
[63] A. Lapworth, L. K. Pearson, and E. M. Mottram, *Biochem. J.*, 1925, **19**, 7; *A.*, i, 355.
[64] *Compt. rend.*, 1911, **153**, 572, 880.
[65] A. Lapworth and E. M. Mottram, *J.*, 1925, **127**, 1629.

The synthesis of arachidic acid and some other long-chain compounds [66] has revealed the fact that the melting points of methyl and ethyl arachidate and of eicosyl alcohol previously observed are from 7° to 10° higher than the true values now recorded. The regular rise in melting point in the even series of long-chain compounds is important, since it has been shown that from this rise, and other regularities, a crystal structure can be predicted [67] which has been shown by *X*-ray analysis to be correct.[68] The synthesis involved a modification of Bouveault and Blanc's method: Ethyl stearate gave octadecyl alcohol, and ethyl arachidate gave eicosyl alcohol; then, for example, octadecyl iodide was converted into mono-octadecylmalonic acid, which on heating gave arachidic acid.

By a modification of the Krafft method, a number of the higher methyl ketones have been obtained,[69] among which methyl *n*-octadecyl ketone and methyl *n*-nonadecyl ketone are new. Starting, for example, with erucic acid (I), behenic acid (II) was prepared by hydrogenation in the presence of palladium. From this, methyl *n*-heneicosyl ketone (III) was formed, which on oxidation gave heneicosoic acid (IV). The barium salt of this, distilled with barium acetate, gave methyl *n*-eicosyl ketone (V).

$$\underset{\text{(I.)}}{C_{21}H_{41}\cdot CO_2H} \longrightarrow \underset{\text{(II.)}}{C_{21}H_{43}\cdot CO_2H} \longrightarrow \underset{\text{(III.)}}{C_{21}H_{43}\cdot CO\cdot CH_3}$$

$$\text{(IV.)}\ C_{20}H_{41}\cdot CO_2H \longrightarrow C_{20}H_{41}\cdot CO\cdot CH_3\ \text{(V.)}$$

The acid (III) proved to be identical with the heneicosoic acid isolated by Le Sueur and Withers [70] and isomeric, therefore, with the cluytinic acid of Tutin and Clewer.[71] L. J. Simon,[72] in the course of a series of investigations on the oxidation of unsaturated fatty acids by a mixture of sulphuric and chromic acids, finds that complete oxidation of the carbon takes place only if the unsaturated linking is in a terminal position. This applies both to dibasic and to monobasic acids. Δ^{γ}-Pentenoic acid is an exception, and undecenoic acid reacts as though the CH_2 group were not present, which observation seems to call for a revision of the structure assigned to this acid. The deficiency in the carbon completely oxidised amounts to nearly 2 atoms per molecule in the case of straight-chain acids, of which stearic, oleic, elaidic, tariric, taroleic, ketotariric, and others were

[66] N. K. Adam and J. W. W. Dyer, *J.*, 1925, **127**, 70.
[67] N. K. Adam, *Proc. Roy. Soc.*, 1922, *A*, **101**, 528.
[68] A. Müller and G. Shearer, *J.*, 1923, **123**, 2043, 3152, 3156.
[69] G. T. Morgan and E. Holmes, *J. Soc. Chem. Ind.*, 1925, **44**, 108T, 491T.
[70] *J.*, 1915, **107**, 736.
[71] *J.*, 1914, **105**, 559.
[72] *Compt. rend.*, 1925, **180**, 833, 1405; *A.*, i, 505, 778.

studied. In derivatives such as the ethyl esters and glycerides there is a deficiency of nearly 2 carbon atoms for every carbon chain in the molecule.

The difficult question of the drying of oils continues to produce a number of reports. P. Slansky [73] observes that the oxide and carbonate of lead or calcium have a far greater effect on the drying of linseed oil than the sulphate. He explains this by a development of the hypothesis of Harkins and Langmuir on the polar distribution of the molecules at a liquid surface, whereby the basic catalysts, in virtue of their affinity for the carboxyl groups of the glyceride end of the molecule, direct these groups inward, leaving the unsaturated groups outward, so that these more readily undergo oxidation. An exhaustive study of the autoxidation of linseed oil [74] has confirmed the accuracy of the pioneer work of Mulder on "linoxyn," for which the formula $C_{57}H_{96}O_{20}$ is confirmed. This is the most highly autoxidised product obtainable by Mulder's method and represents 70—80% of the dried oil. Attempts to separate this substance into two or more components failed, and its individuality is postulated. Experiments on the influence of light and temperature on the oxidation seem to show that the temperature is all-important and that the action of light is mainly due to a heating effect.[75]

As to the mechanism of the "drying" of fatty oils by driers, A. Eibner and F. Pallauf [76] conclude that the autocatalytic agent is the aldehyde peroxide primarily formed. The driers are stated, not only to catalyse the formation of such peroxides, but also to take a direct part in the transference of oxygen.

Monosaccharides.

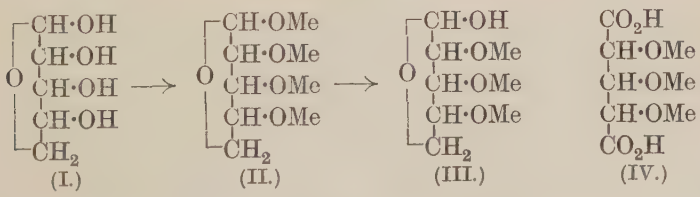
The mixture of sugars (formose) obtained by the action of alkaline condensing agents on formaldehyde has been shown [77] to contain sorbose in addition to *dl*-fructose and a ketopentose. The condensation is said to take place with great ease when formaldehyde is heated in dilute solution under a pressure of 2 atmospheres in the presence of magnesia.[78] Methyl alcohol and formic acid are first produced and the magnesium oxide dissolves. The formation of sugars then begins and is complete in a few minutes. Ketoses are formed in this way, but not aldoses; dihydroxyacetone and a pentose also were recognised among the products.

[73] *Chem. Umschau*, 1924, **31**, 281; *A.*, 1925, i, 114.
[74] G. W. Ellis, *J. Soc. Chem. Ind.*, 1925, **44**, 401, 469T.
[75] *Idem, ibid.*, p. 472T.
[76] *Chem. Umschau*, 1925, **32**, 81; *A.*, i, 777.
[77] W. Küster and F. Schoder, *Z. physiol. Chem.*, 1924, **141**, 110; *A.*, 1925, i, 366.
[78] H. Schmalfuss and K. Kalle, *Ber.*, 1924, **57**, [*B*], 2101; *A.*, 1925, i, 116.

In the Report of last year it was stated [79] that, of the aldoses so far constitutionally examined with respect to their internal oxide rings, galactose and mannose would appear to exist normally as 1 : 5- or amylene oxides. Glucose, to which a 1 : 4- or butylene oxide structure is generally ascribed, remained in doubt, but " should it be drawn into the analogy with galactose and mannose, then the fortuitous terminology of a γ-sugar will acquire a new and general meaning in that such a compound will be one that gives rise on the oxidation of its tetramethyl derivative to a γ-lactone as understood in the ordinary sense," *i.e.*, as one having its lactone ring in the 1 : 4-position. The important observation is now reported by W. N. Haworth [80] that the normal tetramethyl glucose yields on oxidation a δ- and not a γ-lactone, whilst the latter is obtained from the γ-sugar. To glucose, therefore, is assigned the 1 : 5-oxide ring structure, and it may now be said that all aldoses exist normally in the amylene oxide form. This change in the formulation of glucose, if accepted, will necessitate alteration in the oxide ring linking in the case of a large number of structural formulæ assigned to glucose derivatives and carbohydrates based upon glucose.

The above, with other observations recently recorded, emphasises the necessity for obtaining independent evidence for the internal structure of each individual sugar or sugar derivative. Examination of both normal and γ-type of compounds has shown that the same 1 : 5-oxide linking is present in tetramethyl γ-fructose,[81] the normal sugars trimethyl xylose and tetramethyl galactose and probably tetramethyl mannose. The γ-derivatives of galactose, on the other hand, are of the 1 : 4-oxide structure.

In extension of these researches to the pentoses, it has now been shown [82] that the normal stable derivatives of arabinose are of the amylene-oxidic type (II) and in all probability the same structure applies to the free pentose (I).



The evidence was obtained by oxidation of the trimethyl arabinose

[79] *Ann. Report*, 1924, p. 73.
[80] *Nature*, 1925, **116**, 430; *A.*, i, 1133; *J.*, 1926, 89.
[81] W. N. Haworth and W. H. Linnell, *J.*, 1923, **123**, 294.
[82] E. L. Hirst and G. J. Robertson, *J.*, 1925, **127**, 358.

(III), which gave, in quantitative yield, trimethyl glutaric acid (IV). The results of the critical study of the methylation process carried out during the past few years show that the oxide linking of a normal methylaldoside remains unchanged during methylation, so that it may be argued that the unsubstituted α- and β-methylarabinosides, from which the fully methylated derivatives are prepared, will also contain the same type of linking. A new derivative, trimethyl β-methylarabinoside, m. p. 46—48°, was shown to have the same type of oxide linking as the corresponding α-derivative discovered by Purdie and Rose.[83] These derivatives are shown to be interconvertible forms of normal α- and β-trimethyl methylarabinoside. The presence of isomerides with a different oxide ring structure was also indicated.

Derivatives of *l*-arabinose previously known are all dextrorotatory. A new series of lævorotatory compounds has been obtained which have a different oxide ring structure and belong to the class of γ-sugars. Their synthesis was achieved [84] by condensing *l*-arabinose with the methyl-alcoholic hydrogen chloride reagent at 18° instead of 100°. A liquid γ-methylarabinoside ($[\alpha]_D$ −71·3°) results, which is very unstable to potassium permanganate and is readily hydrolysed by dilute acids. On methylation, and hydrolysis with 0·25% acid, trimethyl γ-arabinose was obtained, $[\alpha]_D$−39·5°, the structure of which was determined by its behaviour on oxidation with nitric acid, which gave the lactone of a trimethoxyhydroxyvaleric acid and dimethoxyhydroxyglutaric acid,

$$CO_2H{\cdot}CH(OMe){\cdot}CH(OMe){\cdot}CH(OH){\cdot}CO_2H.$$

These results, coupled with a consideration of Hudson's rule, make a 1 : 3- or a 1 : 4-oxide structure certain and the 1 : 4 is preferred, as the existence of a propylene oxide sugar has hitherto not been substantiated. It would seem to be established, therefore, that in the pentose series the γ-sugars also belong to the butylene oxide type.

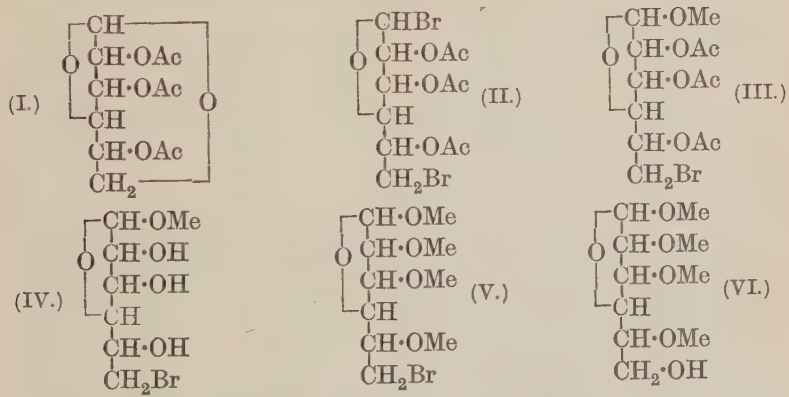
A study [85] of the isomeric tetramethyl galactonolactones and trimethyl arabonolactones still in progress makes it probable that both in the case of galactose and arabinose the original sugars, and the lactones and amides prepared from them, are mixtures of the 1 : 5- and 1 : 4-isomerides. It is pointed out that, whilst galactose and arabinose show such a marked tendency to react in both forms, the 1 : 5 being the normal, glucose and xylose under the same conditions produce only one form. The relationship between the formulæ of the pairs of sugars is suggestive in this connexion.

[83] *J.*, 1906, **89**, 1204.
[84] S. Baker and W. N. Haworth, *J.*, 1925, **127**, 365.
[85] J. Pryde, E. L. Hirst, and R. W. Humphreys, *ibid.*, p. 348.

Galactose.	*Arabinose.*	*Glucose.*	*Xylose.*
H | OH		H | OH	
HO | H	H | OH	HO | H	H | OH
HO | H	HO | H	H | OH	HO | H
H | OH	HO | H	H | OH	H | OH

The structure assigned to the simpler methylated sugars which are utilised as reference compounds in the constitutional study of carbohydrates should obviously be reviewed from time to time in the light of new developments. Of these reference compounds, 2 : 3 : 5(or 2 : 3 : 4)[80]-trimethyl glucose has been examined [86] from this point of view. Its structure forms the key to the constitution of maltose and β-glucosan, and is of importance in connexion with the chemistry of starch. Part of the evidence on which its existing constitution has been based rested on the oxidation reactions with nitric acid, which experience has shown to be not entirely trustworthy.

The new synthesis, however, which was designed to produce a methylated glucose with unsubstituted hydroxyl groups definitely in the terminal positions 1 and 6, entirely confirms the structure previously employed. Evidence of the correctness of the constitution assigned to β-glucosan was also obtained. Triacetyl glucosan (I) was converted into a triacetyl dibromoglucose by Karrer's process, identical with that obtainable from penta-acetyl glucose and therefore having formula (II). The succeeding stages may be represented structurally as follows :



(VI) proved identical with the trimethyl β-methylglucoside obtained directly from the trimethyl glucose which was the object of criticism. β-Glucosan was converted into trimethyl glucose as previously recorded. The sugar, on acetylation, gave trimethyl glucose diacetate, which, with hydrogen bromide, gave trimethyl

[86] J. C. Irvine and J. W. H. Oldham, *ibid.*, p. 2729.

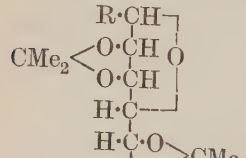
acetyl glucose bromohydrin, and this by the action of sodium methoxide was converted into trimethyl β-methylglucoside identical with (VI) above. The formula for β-glucosan employed in (I) above is thus verified.

A new synthesis of alkylglucosides has been achieved by E. Pacsu,[87] who finds that a mixture of α- and β-methylglucosides is obtained when *d*-glucosedibenzylmercaptal is heated with a methyl-alcoholic solution of mercuric chloride. The mercaptal can also be converted [88] by methyl ethyl ketone in the presence of copper sulphate into a *γδ-iso*butylidene ether, and this compound on suitable treatment yields monomethyl-*d*-glucosedibenzylmercaptal. The latter, by the action of the ethyl alcohol and mercuric chloride, gives the ethyl ether of monomethyl *d*-glucose, from which 4-methyl *d*-glucose, m. p. 156°, is obtained. The constitution of this is deduced from its non-identity with 2-, 3-, or 6-methyl glucose. Trimethylglucosedibenzylmercaptal, by treatment with the methyl-alcoholic mercuric chloride reagent followed by hydrolysis, gave 4:5:6-trimethyl *d*-glucose (I). This represents a case of the presence of a propylene oxide ring, evidence for which was found in its ability to condense with acetone and to give a phenylhydrazone.

(I.) $\overset{\frown\!\!\frown}{\mathrm{CH(OH)\cdot CH(OH)\cdot CH\cdot CH(OMe)\cdot CH(OMe)\cdot CH_2\cdot OMe}}$ (O bridge)

A further study [89] of the acetone sugars has shown that an amino-hexose can be obtained from galactose di*iso*propylidene ether by the action of liquid ammonia followed by the removal of the *iso*-propylidene groups, although the position of the amino-group has not been definitely determined. Di*iso*-propylidene mannose [90] is similarly converted into di*iso*propylidenemannosylamine (II; R = NH_2). This compound, on heating, is transformed into a secondary amine, $(C_{12}H_{19}O_5)_2NH$, the existence of which, coupled with the observation that dimethyl-amine reacts towards di*iso*propylidene mannose in the same way as ammonia, makes it improbable that the primary amine contains the basic group in an 1 : 4-bridge. The constitution of di*iso*propyl-idene mannose is now represented by the formula (II) above (R = OH) instead of that previously given.[91]

(II.)

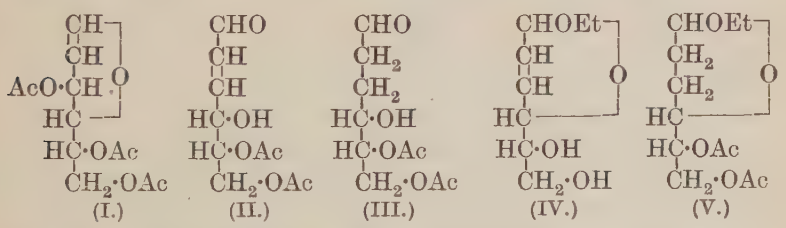


Under the action of triphenylmethyl chloride in anhydrous pyr-

[87] *Ber.*, 1925, **58**, [*B*], 509; *A.*, i, 515.
[88] *Idem*, *ibid.*, p. 1455; *A.*, i, 1242.
[89] K. Freudenberg and A. Doser, *ibid.*, p. 294; *A.*, i, 366.
[90] K. Freudenberg and A. Wolf, *ibid.*, p. 300; *A.*, i, 367.
[91] *A.*, 1923, i, 1179.

idine, reactive hydrogen atoms present in the sugars and certain hydroxy- and amino-acids are replaced by the triphenylmethyl residue.[92] *d*-Glucose, for example, yields triphenylmethyl-α-*d*-glucose, in which the triphenylmethyl group is probably attached at the 6-carbon atom; ethyl β-hydroxypropionate gives ethyl β-triphenylmethyloxypropionate, and carbamide yields bistriphenylmethylcarbamide, a compound remarkably resistant to the action of alkali hydroxide.

Triacetylglucal (I) is converted on boiling with water into a diacetyl derivative (II). This compound combines with two atoms of bromine, but on treatment with hydrogen in the presence of platinum black it takes up four atoms of hydrogen. It has remained uncertain whether this diacetyl compound was a direct derivative of glucal or an isomeric conversion product (see below). M. Bergman,[93] who had advanced the view that a rearrangement of the glucal nucleus takes place on boiling with water and had therefore used the term diacetyl-ψ-glucal for the diacetate formed, now advances further evidence in support of this view. It is found that with palladium-black diacetyl-ψ-glucal forms first a crystalline dihydro-ψ-glucal diacetate (III), which on further reduction gives a *d*-hexane-αδεζ-tetrol diacetate. Both diacetyl-ψ-glucal and the dihydro-derivative (III) react with ethyl orthoformate to give ethyl *cyclo*acetals (IV and V). Compound (V) on hydrolysis yields the



same α-2 : 3-bisdeoxyglucose ethyl *cyclo*acetal as is obtained by the reduction of (IV) with palladium-black.

Glucosides.—Glycerol glucoside, first obtained by E. Fischer[94] by saturating a glycerol solution of glucose with hydrogen chloride, can be obtained more easily by limiting the acid concentration to 0·25% and heating to 100°.[95] The constitution of this compound was established by methylation, which gave a hexamethyl glycerol glucoside. On hydrolysis, this gave 2 : 3 : 5 : 6-tetramethyl glucose together with a dimethyl glycerol identified as αβ-dimethoxy-

[92] B. Helferich, L. Moog, and A. Jünger, *Ber.*, 1925, **58**, [*B*], 872; *A.*, i, 790.
[93] *Annalen*, 1925, **443**, 238; *A.*, i, 887.
[94] *Ber.*, 1894, **27**, 2483.
[95] H. S. Gilchrist and C. B. Purvis, *J.*, 1925, **127**, 2736.

γ-hydroxypropane. The parent glucoside is therefore represented by the formula

$$CH_2(OH)\cdot CH(OH)\cdot \underset{\llcorner\!\!\!-\!\!\!-\!\!\!-

199·8°, prepared for comparison, and whilst, on hydrolysis, the latter derivative gave a 73% yield of 2 : 3 : 5 : 6-tetramethyl glucose, the ether of the new sugar gave only 17·5%. The rotation of the new saccharide agrees fairly well with the value calculated by Hudson for αβ-trehalose ($[\alpha]_D^{20°}$ + 70°), but there is not at present sufficient evidence to decide its identity.

Work on similar lines has been carried out [2] on the galactosidoglucose first prepared in 1902 by E. Fischer and E. F. Armstrong,[3] by the action of sodium alkyloxide on a mixture of dextrose and acetochlorogalactose. The product has generally been regarded as identical with melibiose and the synthesis would thus stand as the earliest accomplished among the disaccharides. The new investigation shows that the octamethyl derivative of the synthetic product is not identical with melibiose octamethyl ether, which has now been prepared for the first time and proved to be, unlike the ether of the synthetic product, crystalline, with m. p. 98·5°. The physical constants of the synthetic octamethyl ether agree closely with those of lactose octamethyl ether and on hydrolysis 2 : 3 : 4 : 6-tetramethyl galactose is obtained, which shows that the galactose components in lactose and in the galactosidoglucose are identical. On the other hand, the glucose component of the latter, isolated as a trimethyl glucose, was not the same as that from lactose, so that the identity of the new sugar with lactose cannot be maintained.

Polysaccharides.

By the oxidation of amylodextrin with bromine in the presence of barium carbonate, V. Syniewski [4] has obtained an amylodextrinic acid, $C_{216}H_{348}O_{198}$, which has reducing properties equivalent to 23·24% of maltose. The barium and lead salts indicate that the new acid has a basicity of twelve, a result which is also in agreement with the composition found for the hydrazide. The following formula is assigned to the acid,

$$[(C_{18})\{>\cdot(C_6)\text{—}O\text{—}\overset{\text{┌———O———┐}}{CH}\cdot[CH\cdot OH]_2\cdot CH\cdot CH(OH)\cdot CO_2H\}_3]_4$$

this being based upon the author's formulation of amylodextrin, $C_{216}H_{372}O_{186}$ (which is formed from starch, $C_{216}H_{360}O_{180}$, by the addition of 6 molecules of water), first suggested [5] in 1902, *viz.*, $[(C_{18})\{>(C_{12})\}_3]_4$, where C_{18} represents an amylogen residue, C_{12} maltose, and > union with the carbonyl linking. From this formula it would appear that glycuronic acid residues should be present in the

[2] H. H. Schlubach and W. Rauchenberger, *Ber.*, 1925, **58**, [*B*], 1184; *A.*, i, 888.

[3] *Ber.*, 1902, **35**, 3146.

[4] *Annalen*, 1925, **441**, 277; *A.*, i, 369.

[5] *Ibid.*, 1902, **324**, 212; *A.*, 1903, i, 69.

new acid equivalent to 34·6% of glycuronic anhydride. Experiment showed that 5·2% of furfural was actually obtained, which corresponds to 34% of glycuronic anhydride. This observation leads to the suggestion that the glycuronic acid of the animal body is derived, not from the oxidation of the primary alcoholic group of dextrose, but by the hydrolysis of an oxidation product of glycogen similar to amylodextrinic acid.

The author's formula for starch, given in condensed form above, is based upon a union of four amylogen complexes. Amylogen is represented as

$$\begin{array}{l}(C_6)\cdot\alpha\cdot(C_6)\cdot\gamma\cdot(C_6)\\ \beta\left|\begin{array}{l}\diagdown\!\!\!\!\diagup\,\beta\\ \diagup\!\!\!\!\diagdown\,\beta\end{array}\right.(C_6)\cdot\alpha\cdot(C_6)\cdot\gamma\cdot(C_6)\\ (C_6)\cdot\alpha\cdot(C_6)\cdot\gamma\cdot(C_6)\end{array}$$

the letters α, β, and γ indicating linkings of these orders, and it was predicted that under exclusively α-carbonyl hydrolysis a non-reducing "limit dextrin I" would be formed. V. Syniewski [6] has now discovered an almost purely α-carbonyl-hydrolytic agent in the diastatic enzyme of ungerminated barley. Under its action amylodextrin is rapidly converted into maltose (64%) and the new "limit dextrin I," $C_{72}H_{132}O_{66}$. This substance does not reduce Fehling's solution and gives a blue colour with iodine, this property differentiating it from the products of the action of malt diastase on amylodextrin. With malt extract, it undergoes β-hydrolysis, giving the reducing "limit dextrin I" identical with the achroodextrin of Lintner. Acetylation shows that forty-eight hydroxyl groups enter into reaction and considerations based upon the author's formula for amylodextrin lead to the conclusion that six of the remaining oxygen atoms are present in α-carbonyl linkings and twelve in β-carbonyl linkings. Its formation is expressed by the equation:

$$C_{216}H_{372}O_{186} + 12H_2O = 12C_{12}H_{22}O_{11} + C_{72}H_{132}O_{66}.$$

The polyamyloses isolated by Pringsheim and others from potato starch have been classified by him ("Die Polysaccharide," 1923, p. 167) into an α- and a β-series. The former includes a hexa-amylose, $[(C_6H_{10}O_5)_2]_3$, and a tetra-amylose, $[(C_6H_{10}O_5)_2]_2$; the latter, a hexa-amylose, $[(C_6H_{10}O_5)_3]_2$, and a triamylose, $(C_6H_{10}O_5)_3$. Although the letters α- and β- were not intended to have any constitutional significance, yet by a coincidence α-hexa-amylose is found to belong to the α- series and αβ-hexa-amylose, which is regarded by Ling and Nanji as identical with Baker's α-amylodextrin, falls among the members of the β-series.[7] The suggestion of Pringsheim is that starch and the amyloses consist of basal units (shown

[6] *Annalen*, 1925, **441**, 285. [7] *J.*, 1923, **123**, 2669.

in round brackets above) polymerised to the varying degrees shown within the angular brackets, the units being held together by subsidiary valencies. R. Kuhn [8] considers that neither the polyamyloses nor the hexosans can be considered with certainty to be the fundamental units of the starch molecule. The lengthy paper in which the arguments are advanced contains the observation that by the action of maltase-free amylase (from green and kilned malt) on starch or amylose the whole of the maltose formed is of the β-form. Taka-diastase and pancreatic amylase, however, yield a maltose the mutarotation graph of which indicates the initial formation of the α-form of maltose. The amylases may thus be divided into α- and β-groups according to the form of maltose initially produced.

The use of biological methods under exactly controlled conditions has led, at the hands of Ling and Nanji,[9] to definite advances in our knowledge of starch. These authors find that some of the starches, *e. g.*, potato starch, consist entirely of amylose (the inner portion of the granule) and amylopectin (the outer portion) and that, if so, these constituents are present invariably in the proportions amylose 66·6%, amylopectin 33·3%. This ratio of 2 : 1 is also found to subsist in the case of starches, *e.g.*, rice starch, which do not consist entirely of amylose and amylopectin. They are able to explain the failure of other workers, *e.g.*, Pringsheim and Wolfsohn,[10] to obtain anything approaching such a high proportion of amylose by the results of a histological investigation of the starch granules, which showed that, whilst some 25% of the " amylose " exists as a crystalloid phase, forming a core round the hilum of the granule which is readily extracted by water and dilute acids, the remainder is present in a colloidal phase, dispersed uniformly through the amylopectin layers. This portion is so strongly adsorbed as to resist extraction. Treatment with barley diastase at 50°, however, converts the amylose into maltose and the amylopectin into αβ-hexa-amylose.

Certain starches, however, notably those of barley, wheat and rice, when treated with barley diastase in this way, leave a residue, amounting to about 7% in the case of wheat starch and 15% in that of rice starch,* which has the properties of a hemicellulose. Ling and Nanji, who prefer the term amylo-hemicellulose,[11] communicate the interesting discovery [12] that this polysaccharide derivative

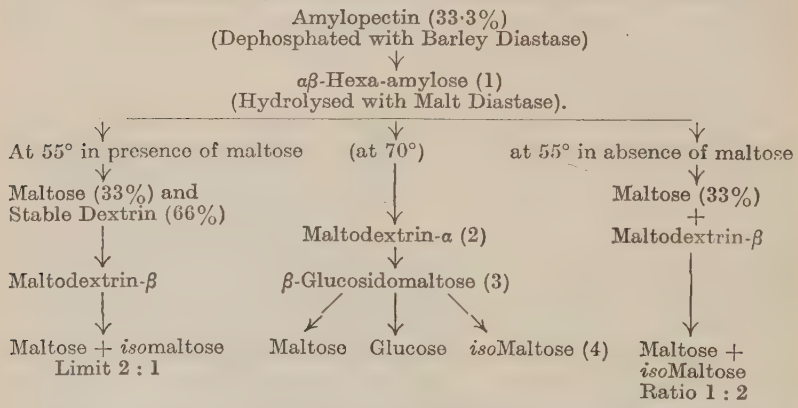
[8] *Annalen*, 1925, **443**, 1; *A.*, i, 636.
[9] *J.*, 1925, **127**, 629.
[10] *Ber.*, 1924, **57**, [*B*], 887.
[11] Compare S. B. Schryver, *Biochem. J.*, 1923, **17**, 493.
[12] *J.*, 1925, **127**, 625; *Z. physiol. Chem.*, 1924, **137**, 265.

* The proportions actually existing in the starch are found by Ling and Nanji to be approximately 10% for wheat and 20% for rice (*loc. cit.*, p. 656).

is the calcium-magnesium, or the iron, salt of a silicic ester (compare also lichenin). It is a white powder with a fairly definite silica content of 0·8 to 0·9%. The sugar produced by its complete hydrolysis is exclusively maltose, which proves amylohemicellulose to be a derivative of α-hexa-amylose.

The researches of Ling and Nanji on amylopectin and its derivatives are summarised,[13] and may be followed by reference to the following scheme.

The Hydrolysis of Starch with Barley and Malt Diastase.



β-*Glucosidomaltose*.—The trihexose [14] previously obtained from amylopectin has now definitely been shown to have this constitution. Taking advantage of an observation of Neuberg and Saneyoski [15] that the osazones of the bioses are capable of being hydrolysed by enzymes, the action of the α- and β-enzymes, maltase and emulsin, on the osazone of the trihexose was examined; under the action of maltase the products were glucosazone and *iso*maltose, under that of emulsin they were maltosazone and glucose. The constitution of the trihexose is therefore β-glucosidomaltose,

$$C_6H_{11}O_5\cdot O\cdot C_6H_{10}O_4\cdot O\cdot C_6H_{11}O_5.$$

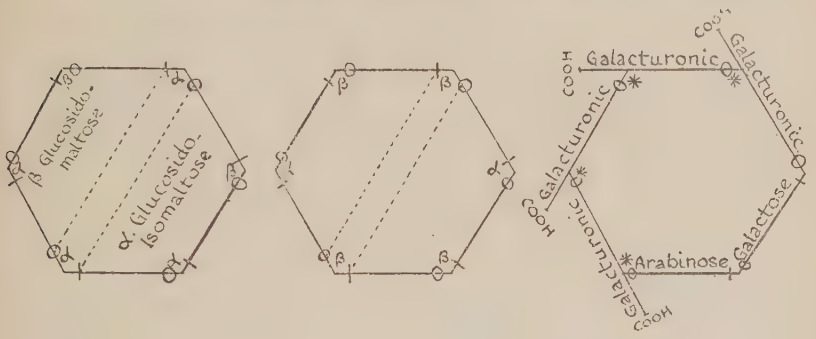
The structure of *iso*maltose is at present uncertain, that previously suggested, *viz.*, 1 : 5-glucosidoglucose, belonging to cellobiose. The β-linkings used in the formulæ, *e.g.*, (I) and (II) on p. 93, to represent the *iso*maltose unit may either be 1 : 5 or 1 : 4, and the oxidic ring, butylene or amylene-oxide, respectively.

The structure (I), previously assigned to αβ-hexa-amylose, demands the production of the two trihexoses named on the figure. Since the action of malt diastase at 70° results exclusively in the production of β-glucosidomaltose, a modification is necessary, and of the structures which could yield this trihexose as sole product, formula

[13] *J.*, 1925, **127**, 636. [14] Ling and Nanji, *J.*, 1923, **123**, 2666.
[15] *Biochem. Z.*, 1911, **34**, 44.

(II) is preferred, since it is in agreement also with observations on the stable dextrin now to be described.

In this connexion the authors have shown that, whilst α-hexa-amylose is converted by malt or barley diastase at 50° into maltose, without the formation of intermediate products, αβ-hexa-amylose, treated with malt diastase at 70°, gives β-glucosidomaltose. A further set of observations [16] shows that αβ-hexa-amylose, treated with malt diastase at lower temperatures, *viz.*, between 30° and 70°, and in presence or absence of maltose, gives rise to a series of products intermediate between it and β-glucosidomaltose. The nature and formation of these products will be seen by reference to the scheme given above. The term maltodextrin is applied to all the non-crystalline, intermediate products of the action of diastase on



(I.) αβ-Hexa-amylose. (II.) (III.) Pectic acid.

starch possessing cupric-reducing power. The "stable dextrin" shown in the scheme is regarded by Ling and Nanji as a maltodextrin of the highest type. Maltodextrin-α, $C_{36}H_{62}O_{31}$, and maltodextrin-β, $C_{24}H_{42}O_{21}$, were isolated by Ling and Baker in 1895.[17] These three dextrins are now considered to be the only distinct types of maltodextrin existing.

The "stable dextrin" was first obtained by Brown and Morris in 1885 [18] as an invariable product of the hydrolysis of starch paste by malt diastase at 50°. The determination of its constitution is a problem of great importance both from a chemical and a technical point of view. In order to attack this problem, Ling and Nanji studied the origin of the dextrin, the conditions of its formation, and the nature of its products of hydrolysis with malt diastase.

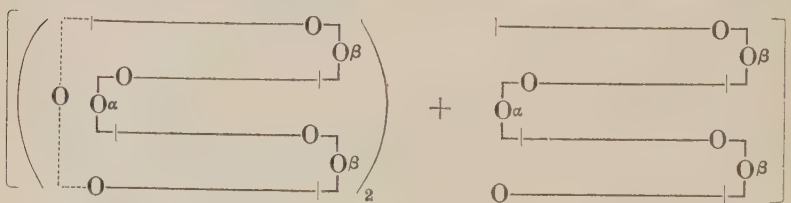
The stable dextrin was prepared in nearly theoretical yield by the action of malt diastase on starch at 40°. Amylopectin or αβ-hexa-amylose, when treated with this enzyme between 30° and

[16] *Loc. cit.*, p. 636.

[17] *J.*, 1895, **67**, 703; 1897, **71**, 517.

[18] *J.*, 1885, **47**, 543.

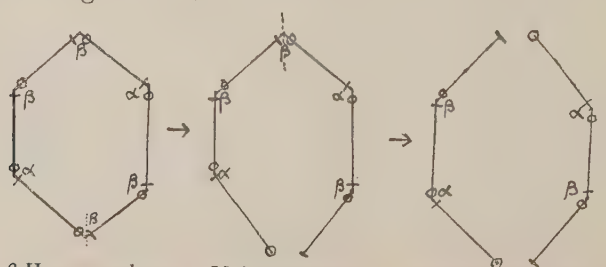
70° in the presence of excess of maltose, is converted one-third into maltose and two-thirds into stable dextrin. In the absence of maltose, however, αβ-hexa-amylose itself gives no stable dextrin. The molecular weight of this dextrin is of the order of 1923 and its reducing power R 14. The first factor would agree with the formulation of the dextrin as an open-chain compound of 12 hexose residues. The second, on the other hand, would exclude a completely closed-chain structure. The considered view of the authors is that it is partly composed of a closed-chain and partly of an open-chain structure, the basal molecule of both being the same. They regard it as a mixture, possibly a co-ordinated mixture, of two components, one of which is an open-chain compound identical with the maltodextrin β of Ling and Baker (M.wt. 693), the other a closed-chain compound of very much higher molecular weight with the same C_{24} unit representing its closed-chain basal structure. Considerations based upon the reducing power of the various products obtained upon fission lead to the conclusion that αβ-hexa-amylose must have the formula (II) given above and that maltodextrin-β must possess the skeletal formula (IB) in the annexed scheme :



(IA) (IB)

The stable dextrin thus consists of two molecules of a polymerised tetra-amylose corresponding to maltodextrin-β (IA), united with one molecule of maltodextrin-β (IB).

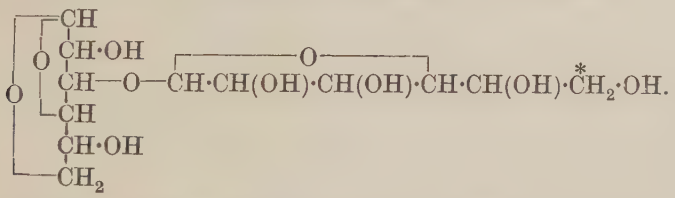
The constitution of maltodextrin-α was determined by similar considerations, coupled with the fact that it is formed when starch is hydrolysed by malt diastase at 70°. It must be regarded as an intermediate product of the degradation of αβ-hexa-amylose to β-glucosidomaltose. Its constitution and relationships are shown in the following scheme :



αβ-Hexa-amylose. Maltodextrin-α. β-Glucosidomaltose.

By the polymerisation of β-glucosan (1 : 6-anhydroglucose) Pictet [19] has obtained four synthetic dextrins, these being di-, tetra-, hexa-, and octa-glucosans, respectively, no polymeride containing an odd number of units being observed. Irvine and Oldham,[20] by using zinc as a catalyst, have now prepared three new products, apparently a hepta-, a tetra-, and a tri-glucosan, which, in contrast with those described by Pictet, readily yield a triacetate and contain three hydroxyl groups for each C_6 unit. But these hydroxyl groups are not uniformly distributed as they are with the isomeric substances cellulose and hexa-amylose. The latter yield 2 : 3 : 6-trimethyl glucose and no other sugar. The synthetic dextrins are constituted on a different model from that of these natural polysaccharides, for on similar methylation treatment they give methyl-glucosides of 2 : 3 : 5 : 6-tetramethyl glucose, 2 : 3 : 5-trimethyl glucose, and a dimethyl glucose which must be either 2 : 3- or 2 : 5-dimethyl glucose. Synthetic di(trimethylglucosan) gave the di- and the tetra-methyl glucose in the ratio of equal molecules, and the poly(trimethylglucosan) gave the di-, tri-, and tetra-methyl glucose in equal molecular proportion.

There is now, therefore, a series of polymerides from mono- to octa-glucosan with the exception of the penta-form. Monoglucosan yields 2 : 3 : 5-trimethyl glucose only, diglucosan yields a mixture from which trimethyl glucose is absent. The others all yield this sugar in equimolecular proportion with other homologues. A consideration of the mechanism of the polymerisation is based on the significant fact that all the polyglucosans yield a tetra- and a dimethyl glucose. The first action is the conversion of glucosan into glucose, and the dimeride must then be formed, so that there are four hydroxyl groups in one glucose residue to two in the other. The following structure is provisionally assigned to diglucosan :



In the case of triglucosan, the glucose residue is shown to be attached at the terminal carbon atom C*.

Pectins.—A distinct advance in our knowledge of the constitution of this group of plant products has resulted from the observation that when the linking of the constituent units of polysaccharides is other than 1 : 6, acids of the nature of conjugated glycuronic acid are

[19] *Helv. Chim. Acta*, 1918, **1**, 226. [20] *J.*, 1925, **127**, 2903.

formed by oxidation in alkaline or neutral solution.[21] Thus lactose gives finally galacturonic acid, and sucrose glycuronic acid. These " uronic " acids should be formed from any polysaccharide in which the terminal carbinol group is free, and the potential reducing group linked. The pectins are known to be partly constructed of such galacturonic acid units, and a method for the estimation of " uronic " acids based upon their quantitative decarboxylation is described. Until recently, it was considered that there were three pectin substances in plants, *viz.*, the insoluble parent compound, protopectin, which, during the ripening process, gave rise to the soluble pectinogen, and this, on further de-esterification, was converted into pectic acid. It is now shown that iron is a more important constituent of these substances than calcium–magnesium and that protopectin is, in all probability, nothing but pectinogen in loose combination with metallic ions, chiefly iron ions. There would then be two pectin substances only, pectinogen and pectic acid, and a critical study of the evidence leads the authors to conclude that the relation between them is such that the only change involved in the formation of pectic acid lies in the de-esterification of pectinogen and that the basal molecules are identical. Since tetragalacturonic acid has been obtained by the hydrolysis of pectic acid, the basal molecule cannot be $C_{17}H_{24}O_{16}$ as suggested by previous workers,[22] whilst the fact that pectic acid contains 70·56% of galacturonic acid suggests that the basal molecule is composed of six units, four of which are galacturonic acid units, the others being an arabinose and a galactose residue.

There will thus be four free carboxyl groups in pectic acid. Pectinogen, which contains 6 to 9% of methoxyl groups, is regarded as the di- or tri-methyl ester. A schematic formula embodying these opinions will be found on p. 93 (III), in which the sign + represents a carbinol group, ⊙ a carbonyl group, and * a linking other than 1 : 6. The similarity of this structure to that of the basal molecule of the constituents of the starch granule is noteworthy.

In criticism of the statement that there are only two pectic substances, a microscopical and chemical study has led M. J. Carré [23] to the conclusion that protopectin (preferably called pectose) is chemically different from the pectin to which it gives rise and that both are normally present in ripe fruit.

Lignin.—The lignin isolated from flax by resolution with sodium hydroxide was found [24] to have the formula $C_{45}H_{48}O_{16}$ and to contain in this unit one active aldehydic group and nine hydroxy-groups,

[21] D. N. Nanji, F. J. Paton, and A. R. Ling, *J. Soc. Chem. Ind.*, 1925, **44**, 253T.

[22] S. B. Schryver and D. Haynes, *Biochem. J.*, 1916, **10**, 539.

[23] *Biochem. J.*, 1925, **19**, 257.

[24] *Ann. Report*, 1924, p. 87.

of which four were methylated. The application of similar methods of investigation to the lignins obtained from various woods—poplar, birch, ash, spruce, larch, and pine—has shown [25] that all these lignins are derivatives of the same hydroxy-compound,

$$C_{38}H_{30}O_4(CO)_2(CHO)(OH)_9,$$

for which the name lignol is suggested. They differ only in the number of methoxyl groups present, which varies between 3 and 5.

The isolation of lignin as sodium lignate has also been employed by M. M. Mehta,[26] who finds that with 4% sodium hydroxide solution, under 10 atmospheres pressure, the lignin is removed from all plant materials in 1 hour. The proportion of lignin found by this method in a number of woody tissues is very much lower than that obtained by the hydrochloric acid method, but it is claimed that the product represents more nearly the original lignin of the plant.

This lignin melts at 170° and has an iodine value of 139 and an acid value of 477. It is soluble in alcohol and dilute alkalis. The author considers that lignocellulose is a compound of a glucosidic type, the phenolic hydroxyl group of lignin condensing with the carbonyl group of the reactive form of cellulose believed to be present in woody tissues.

If hydrochloric acid (*d* 1·22) is allowed to act for a short time only on the wood substance, a lignin of a new type is obtained.[27] It is a light yellow powder, insoluble in the usual solvents, but soluble in trichloroacetic acid, from which it is reprecipitated by water in a form soluble in alkalis, acetone, etc. Heated at 200°, it gives some 60% of its weight as a sublimate consisting of vanillic acid with a little vanillin, but these products are the result of oxidation, as, in an inert atmosphere, neither is produced. The residue seems to be a decomposition product of dextrose, which supports the conclusion, previously drawn, that lignin is a 1 : 3 : 4-benzene derivative bound to a glucoside residue. It is regarded as a colloidal coniferin complex, evidence for this view being obtained from a comparison of the action of various reagents on lignin and on coniferin, respectively.

The investigation of the lignosulphonic acid obtained from spruce wood by the action of sulphurous acid, in the absence of a base, at 100°, reported last year [28] has led to a number of publications on this simple method for the resolution of lignified tissues.

[25] W. J. Powell and H. Whittaker, *J.*, 1925, **127**, 132.

[26] *Biochem. J.*, 1925, **19**, 958.

[27] K. Kürschner, *Brennstoff-Chem.*, 1925, **6**, 117, 208, 304; *B.*, 1925, 912; *Mikrochem.*, 1925, **3**, 1; *A.*, i, 890.

[28] *Ann. Report*, 1924, p. 87.

The C_{26} acid so obtained [29] was stated by P. Klason [30] to be a mixture of a dibasic and a monobasic sulphonic acid, $C_{40}H_{40}O_{12},2H_2SO_3$ and $C_{40}H_{40}O_{12},H_2SO_3$, respectively. He finds, however, that under the mildest possible conditions of the action of sulphurous acid an acid, $C_{30}H_{30}O_9,H_2SO_3$, is obtained which he considers to be the correct formula for this lignosulphonic acid. Under drastic treatment with sulphurous acid, a product was isolated (as the β-naphthylamine salt) which appears to be the sulphonic acid of coniferylaldehyde. Provisionally, therefore, α-lignosulphonic acid is regarded as a sulphonate of polymerised coniferylaldehyde. The opinion of Klason that his aldehydic α-lignin, $C_{20}H_{20}O_6$, reacts with sulphurous acid by reason of the presence of an acraldehyde or similar unsaturated aldehydic residue has been examined by E. Hägglund,[31] who finds that, with acraldehyde itself, the sulphonic acid group attaches itself to the β-carbon atom relative to the aldehydic group, and not the α-one. It is shown that cinnamaldehyde undergoes a condensation of the aldol type with hydrochloric acid, and some of the anomalies observed in connexion with the reaction of lignosulphonic acids with β-naphthylamine may be explained by the probability that α-lignosulphonic acid may undergo a similar aldol condensation. The addition of 0·1 to 0·5% of ammonia to the 7% sulphurous acid solution improved the process of resolution of lignified fibres out of all proportion to its active mass.[32]

Plant Cuticles.—Some confusion has arisen by the use of the terms adipocellulose and cutocellulose for cork and cuticle, respectively. It is shown [33] that the outer layer of the cuticle of plants (as distinct from the cutinised layer) does not contain cellulose, and the term plant cuticle is preferred. The cuticle from *Agave americana* has been carefully examined with a view to a comparison with the (ancient) cuticle found in bituminous coals. After suitable purification, the product, for which the term *cutin* is suggested, appeared to be definite. By the action of alcoholic potash two acids were obtained from it: $C_{26}H_{50}O_6$, cutic acid, and $C_{13}H_{22}O_3$, cutinic acid, the former being in greater proportion. The oleocutic acid described by Fremy appears to be a mixture of these two semi-liquid acids.

Cellulose.—The formation between cellulose and alkali hydroxides of definite compounds of the type $(C_6H_{10}O_5)_2,M{\cdot}OH$ is now

[29] C. Dorée and L. Hall, *J. Soc. Chem. Ind.*, 1924, **43**, 257T; *A.*, 1924, i, 1048.

[30] *Ber.*, 1925, **58**, [*B*], 375, 1761; *A.*, i, 371, 1246.

[31] *Cellulosechem.*, 1925, **6**, 29; *A.*, i, 643.

[32] C. F. Cross and A. Engelstad, *J. Soc. Chem. Ind.*, 1925, **44**, 267T.

[33] V. H. Legg and R. V. Wheeler, *J.*, 1925, **127**, 1412.

regarded as established. These compounds are shown to be stable only in aqueous alkaline solutions of medium concentrations and W. Vieweg,[34] who has re-examined the question, proves that the compounds do not exist in the aqueous-alcoholic solutions usually employed for their investigation. These conclusions are confirmed by E. Heuser,[35] who considers that the existence of the compound, $(C_6H_{10}O_5)_2$,NaOH, in solutions containing 16—24% of sodium hydroxide is quite definite. That it is a chemical union is supported by the fact that lithium and potassium hydroxides also react with cellulose in the same molecular ratio, $(C_6H_{10}O_6)_2 : M{\cdot}OH$; the compounds are stable, respectively, in solutions containing 9—11% of lithium hydroxide and 25—35% of potassium hydroxide.[36] Strong organic bases also [37] show a similar behaviour, some, such as trimethylsulphonium hydroxide, forming compounds of the molecular ratio 2 cellulose : 1 base; others, such as tetramethylammonium hydroxide, combining in the ratio 3 cellulose : 1 base. With rubidium and cæsium hydroxides, compounds are formed in the ratio $(C_6H_{10}O_5)_2 : M{\cdot}OH$, the cæsium compound being stable in solutions containing 45—60% of cæsium hydroxide. These ratios represent the limit of chemical combination observed, the higher ratio, $C_6H_{10}O_5 : M{\cdot}OH$, indicated originally by Vieweg, not being confirmed. The swelling of the fibres in alkaline hydroxide solutions of various concentrations [38] proceeds up to the point at which the compound is formed. Solutions of alkali hydroxides at the concentration at which the electrical conductivity is at a maximum produce maximum swelling. Ions with lowest atomic volumes are associated with the highest number of water molecules, and the explanation given is that the alkali ion, entering into combination with the cellulose molecule, carries its associated water with it and distends the cellulose. The ionic nature of the alkali–cellulose union is supported by the fact that reaction does not proceed in alcoholic solution. In another memoir,[39] it is also shown that maximum swelling occurs in solutions of the hydroxides corresponding with the fully hydrated ion, although the connexion between maximum swelling and electrical conductivity is not confirmed. Thus with the lithium ion, which is supposed to attract to itself 17 molecules of water, a maximum swelling occurs at 6·6% LiOH, the composition of the solution being 1 molecule

[34] *Ber.*, 1924, **57**, [*B*], 1917; *A.*, 1925, i, 12; *Z. angew. Chem.*, 1924, **37**, 1008; *A.*, 1925, i, 119.

[35] *Z. angew. Chem.*, 1924, **37**, 1010; *A.*, 1925, i, 119.

[36] *Idem, loc. cit.*

[37] F. Dehnert and W. Konig, *Cellulosechem.*, 1925, **6**, 1; *A.*, i, 369.

[38] E. Heuser and R. Bartunek, *ibid.*, p. 19; *A.*, i, 520.

[39] G. E. Collins, *J. Text. Inst.*, 1925, **16**, 123T.

of lithium hydroxide to 17 molecules of water. For the other hydroxides, the corresponding ratios are: NaOH, $12H_2O$ (15·5%); KOH, $7H_2O$ (38%); RbOH, $6H_2O$ (49%). Röntgen spectroscopic methods also have been applied to the study of these problems.[40, 41, 42]

Hess has shown [43] that the chemical structural form of celluloses of all origins, whatever their degree of dispersion or solubility, is practically identical, in cuprammonium solution, with that of normal cotton cellulose, and that in this solution the cellulose molecule reacts in its simplest form, *viz.*, $C_6H_{10}O_5$. The solvent action of cuprammonium solution on cellulose is generally considered to result in the formation of a complex cellulose copper anion, which forms with the cuprammonium kation the salt

$$(C_6H_7O_5Cu)_2,Cu(NH_3)_4.$$[44]

Another investigation supports [45] the view that the greater part of the copper in a solution of cuprammonium hydroxide exists as part of the complex ion $Cu(NH_3)_4^{++}$, and to explain the observations recorded, the interesting hypothesis is advanced that cuprammonium–cellulose solutions are members of the class of colloidal electrolytes typified by the soap solutions. The strong base $Cu(NH_3)_4(OH)_2$ forms with cellulose, functioning here as a weak acid, a soluble basic salt in which the kation is "crystalloidal" and the anion "colloidal." It is proved that each cellulose–hexose unit, $C_6H_{10}O_5$, is associated with one atom of copper. The anionic micelle, consisting of a larger number (n) of condensed hexose groups carrying n negative charges, is, with the n hydroxyl ions, equivalent to n bivalent cuprammonium ions. The "solution" of cellulose, therefore, may be represented by the equation

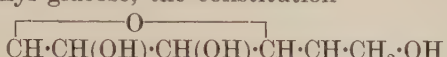
$$(C_6H_{10}O_5)_n + nCu(NH_3)_4(OH)_2 \longrightarrow [Cu(NH_3)_4]_n(C_6H_9O_5)_n(OH)_n + nH_2O,$$

the salt being highly ionised into $nCu(NH_3)_4^{++}$, nOH^-, and $(C_6H_9O_5)_n^-$.

By the optical method, it has been shown that lichenin is not identical with cellulose.[46] Lichenin is depolymerised on heating in glycerol at 240°,[47] giving lichosan the molecular weight of which shows it to be a glucose anhydride, $C_6H_{10}O_5$. It polymerises

[40] J. R. Katz, *Cellulosechem.*, 1925, **6**, 35.
[41] J. R. Katz and H. Mark, *Z. Elektrochem.*, 1925, **31**, 105; *A.*, i, 640.
[42] R. O. Herzog, *Cellulosechem.*, 1925, **6**, 39; *A.*, i, 639.
[43] *Z. angew. Chem.*, 1924, **37**, 993; *A.*, 1925, i, 118.
[44] K. Hess and E. Messmer, *Annalen*, 1924, **435**, 1.
[45] S. M. Neale, *J. Text. Inst.*, 1925, **16**, 363T.
[46] K. Hess, *Z. angew. Chem.*, 1924, **37**, 993; *A.*, 1925, i, 118.
[47] H. Pringsheim, W. Knoll, and E. Kaston, *Ber.*, 1925, **58**, [*B*], 2135; *A.*, i, 1385.

rapidly to lichenin, the Röntgen spectrum of which is identical with that of the original lichenin. Lichosan is therefore probably the parent substance of lichenin. On acetolysis, it gives octa-acetyl cellobiose, and as lichinen itself, on methylation, gives 2 : 3 : 6-trimethyl glucose, the constitution



is assigned to lichosan.

The alkali-soluble form of cellulose, called by its discoverer Cellulose A, has been shown [48] to be capable of methylation up to a methoxyl content of 45% (a trimethyl cellulose requires 45·6%), which is higher than that so far obtained from the ordinary insoluble cellulose. Hydrocellulose also yields a trimethyl derivative apparently identical with trimethyl cellulose A and, like it, forming a colloidal solution in water. Both products, on treatment with methyl-alcoholic hydrogen chloride, yield a trimethyl methyl-glucoside identical with that obtained from insoluble trimethyl cellulose.[49] The product is, however, almost entirely in the α-form and not a mixture of the α- and β-forms as assumed by Irvine and Hirst.[50] An α-configuration is therefore assigned to trimethyl cellulose. Cellulose A forms the best starting point for the preparation of 2 : 3 : 6-trimethyl glucose, the glucoside being obtained from it in a yield of 88%. The authors comment on the remarkable fact that the same trimethyl glucose is obtained from the methyl ethers of such chemically different polysaccharides as cellulose, lichenin,[51] starch,[52] and β-hexa-amylose.[53]

The production of cellobiose through the acetolysis of cellulose has occupied a prominent place in constitutional questions relating to cellulose. W. Weltzein and R. Singer [54] in conjunction with K. Hess find that the action of acetic anhydride, containing 10% of sulphuric acid, on cellulose yields cellobiose octa-acetate, cellodextrin acetates containing cello*iso*biose, and derivatives of the monoses, in approximately equal quantities, whilst with cellulose triacetate the products are the same, but the proportion of cellobiose octa-acetate is very much smaller. An exhaustive fractionation of the cellodextrin acetates was made, resulting in their classification into six groups of varying solubility in alcohol and ether, and with optical rotations, in chloroform solution, ranging

[48] K. Hess and W. Weltzien, *Annalen*, 1925, **442**, 46; *A.*, i, 517.
[49] J. C. Irvine and E. L. Hirst, *J.*, 1923, **123**, 520.
[50] *Loc. cit.*, p. 530. [51] *Helv. Chim. Acta*, 1924, **7**, 366.
[52] J. C. Irvine, *Brit. Assoc. Rep.*, 1922, 17.
[53] J. C. Irvine, *J.*, 1924, **125**, 942.
[54] *Annalen*, 1925, **443**, 71; *A.*, i, 641.

between — 24° and + 20°. The best crystallised fraction of these cellodextrin acetates yielded a cello*iso*biose, which was shown to be identical with that described by Prosiegel and Knoth.

Since cello*iso*biose octa-acetate cannot be transformed into cellobiose octa-acetate under conditions of acetolysis, it is probable that the conversion of cellulose into dextrose takes place through cello-*iso*biose and not directly. Investigations on this point and on the constitution of cello*iso*biose are in progress, for the importance of this sugar as a first degradation product of cellulose-acetolysis is emphasised. If cello*iso*biose and not cellobiose is the primary product of acetolysis, its quantitative formation from cellulose becomes a possibility, which is under examination, and the formula of Irvine, which was based upon a yield of cellobiose of 50%, would need revision. T. Ozawa,[55] by the acetolysis of sulphite wood pulp, claims to have obtained cellobiose octa-acetate in a yield of 90% without any dextrose as a by-product, his conclusion being that cellulose is a complex of polymerised cellobiose units.

Cellulose triacetate has been prepared [56] in well-defined crystals from solutions in tetrachloroethane, the colloid apparently crystallising in combination with the solvent. The mixture of di- and triacetates of which the acetone-soluble cellulose acetate, "cellite," is composed can also be crystallised from hot benzene–alcohol solution, the crystals being stable only in contact with the liquid. After 40 recrystallisations, the cellulose obtained on hydrolysis was identical with the original cellulose, so that the existence of more than one isomeride in natural cellulose is unlikely.

It is remarkable that the study of the oxidation of cellulose has never thrown any light on its constitution. No definite product of oxidation, indeed, can be found in the so-called oxycellulose, which appears to consist of cellulose and cellulose A, with mechanically adherent compounds in minor proportion. The development of carboxyl groups [57] during oxidation, however, requires explanation. An interesting research [58] defines more exactly the nature and formation of the oxycelluloses. It is shown that the oxycelluloses fall into two classes, (*a*) the non-reducing type with a marked affinity for methylene-blue and power of fixing alkalis; coupled with the low reducing power evidenced by small copper number and slight solubility in sodium hydroxide solutions, (*b*) the reducing type with high copper numbers and marked solubility in alkaline solutions, but with low absorptive power for basic dyes and for

[55] *J. Chem. Ind. Japan*, 1924, **27**, 884; *A.*, 1925, i, 234.

[56] K. Hess, *Z. angew. Chem.*, 1924, **37**, 993; *A.*, 1925, i, 118.

[57] K. Hess, *Papier-Fabr.*, 1925, **23**, 122; *A.*, i, 519.

[58] C. Birtwell, D. A. Clibbens, and B. P. Ridge, *J. Text. Inst.*, 1925, **16**, 13; *A.*, i, 234.

alkalis. Oxycelluloses of type (*b*), when boiled with dilute alkalis, become chemically indistinguishable from normal cellulose, whereas those of class (*a*) are not altered by such treatment. The type of oxycellulose produced is dependent on the alkalinity or acidity of the solution, those of type (*a*) being produced under alkaline, those of type (*b*) under acid conditions. A careful study of the variation produced with hypochlorites and hypobromites of increasing hydrogen-ion concentration shows that from p_H 12 to p_H 2·7 there is a rise in the copper number from 0·6 to 3·7 and a fall in the methylene-blue absorption from 2·1 to 0·9, rapid change occurring near the neutral point.

Compounds of Nitrogen and of Sulphur.

The number of papers dealing with compounds containing nitrogen is very large and it is only possible briefly to refer to one or two. By the action of nitric acid on sodium fulminate at — 18°, *iso*cyanilic acid has been prepared for the first time in quantity.[59] It is now shown that the acid is tetrameric, the silver salt being $C_4H_3O_4N_4Ag$. By energetic treatment with thionyl chloride, a substance, $C_4O_2N_4$, is obtained, accompanied by the furoxandicarbonamide of Ulpiani. The substance $C_4O_2N_4$ is the nitroacetonitrile of Steiner. It is now shown to have the constitution of dicyanofuroxan, $\begin{matrix}C(CN):N(:O)\\ \vert \quad\quad >O\\ C(CN)=\!=N\end{matrix}$, and *iso*cyanilic acid itself is deduced to be the dioxime of furoxandialdehyde,

$$\begin{matrix}C(CH:N\cdot OH):N(:O)\\ \vert \quad\quad\quad\quad >O.\\ C(CH:N\cdot OH)=\!=N\end{matrix}$$

The acid was also synthesised from *syn*-chloroglyoxime by the action of sodium hydrogen carbonate, the intermediate substance, $CH(:N\cdot OH)\cdot C:N:O$, polymerising to the ring compound.

A lengthy contribution on the nature of thiocarbamide and the thiuronium salts [60] adduces proof that the acid hydrogen in the salts of thiocarbamides is attached to the sulphur atom. According to the position of the positive charge in the thiuronium ion, the salts may be of the sulphonium, carbonium, or immonium type, *viz.*, $(NR_2)_2C{:}\overset{+}{S}R$, $(NR_2)_2\overset{+}{C}\cdot SR$ or $(NR_2)\cdot SR\cdot C{:}\overset{+}{N}R_2$. These ideas are shown to be improbable and the basic function is probably divided between the two nitrogen atoms, the ionic charge alternating from one to the other. A similar dynamic formula is suggested [61] for the guanidinium ion.

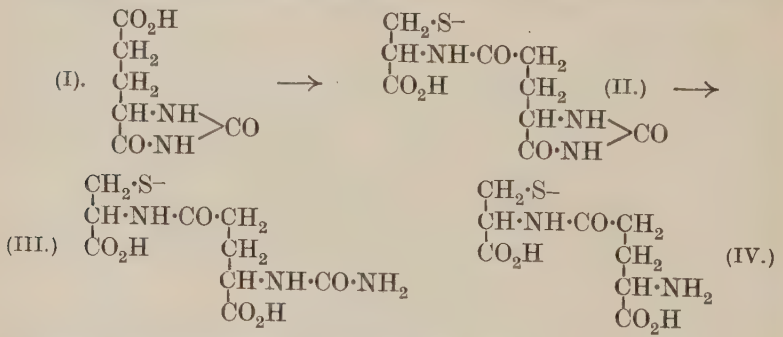
[59] H. Wieland and others, *Annalen*, 1925, **444**, 7; *A.*, i, 1048.

[60] H. Lecher and others, *ibid.*, p. 35; *A.*, i, 1390.

[61] H. Lecher and F. Graf, *ibid.*, 1925, **445**, 61; *A.*, i, 1392; compare *A.*, 1924, i, 1051.

A product of hydrolysis of the proteins hitherto undescribed has been isolated [62] from isinglass. It is a strong base with the formula $C_6H_{14}O_3N_2$, giving a tribenzoyl derivative. The evidence seems to indicate that it is αε-diamino-β-hydroxy-*n*-hexoic acid and the name "oxylysine" is proposed. Its presence has been demonstrated in a variety of protein substances.

A series of investigations [63] on the important biochemical product glutathione has culminated in a brilliant synthesis [64] of this compound. Glutamic acid was converted into the hydantoinpropionic acid (I) by Dakin's method. The acid bromide of this, coupled with cystine dimethyl ester hydrochloride in the ordinary way, gave di(hydantoinpropionyl)cystine (II). Boiling with calcium hydroxide opened the ring with the formation of a uramino-acid (III), which, on treatment with nitrous acid, gave the amino-acid (IV)—glutathione. This product was partly racemised, but a glutathione identical with the natural product was obtained from a



glutamyl monobromide, prepared by the action of phosphorus tribromide on glutamic acid, which was shown to have the constitution $BrOC{\cdot}CH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$. This substance when coupled with cystine dimethyl ester gave diglutamylcystine or glutathione. These methods apply to the synthesis of all dipeptides of the type $\begin{matrix}R\\R_1\end{matrix}\!>\!CH{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$.

CHARLES DORÉE.

[62] S. B. Schryver, H. W. Buston, and D. H. Mukherjee, *Proc. Roy. Soc.*, 1925, *B*, **98**, 58; *A.*, i, 794.

[63] H. E. Tunnicliffe, *Biochem. J.*, 1925, **19**, 194, 199.

[64] C. P. Stewart and H. E. Tunnicliffe, *ibid.*, p. 207.

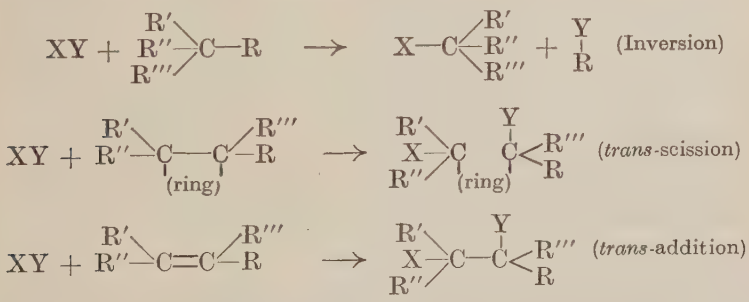
Part II.—Homocyclic Division.

Stereochemistry of Nitrogen, Sulphur, and Arsenic.

Geometrical Isomerism of Oximes.—The customary oxime configurations have long been taken for granted, and therefore the recent suggestion that they require inversion arrests attention.

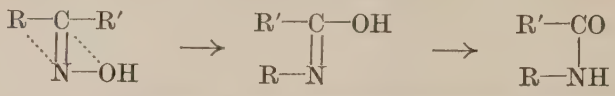
The methods which until recently had been generally accepted are based fundamentally on the theory of preferential *cis*-interaction. Thus Hantzsch's method of orienting aldoximes, which has been employed since 1891, depends on the fact that the acetyl derivative of one geometrical isomeride regenerates the parent oxime on treatment with alkalis, whilst the acetyl derivative of the other loses acetic acid, giving the nitrile; the assumption that elimination can take place from *cis*- but not from *trans*-positions under the conditions employed is arbitrary. Similarly, in ascribing configurations to ketoximes on the basis of the Beckmann change, a *cis*-interchange of radicals is postulated:

It has, however, long been known that preferential *cis*-elimination and *cis*-addition, in spite of its simple mechanical interpretation, is not the rule amongst ethylenic compounds. Indeed, the occurrence of the Walden inversion, proving that in substitution the new group does not necessarily enter at the disrupted bond, appears to establish the possibility not only of *trans*-addition to double linkings but also of *trans*-scission of rings:



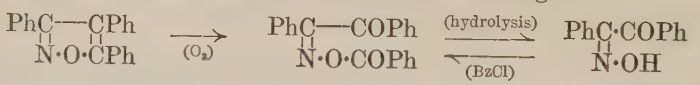
Reversal of *trans*-addition leads to *trans*-elimination, whilst *trans*-interchange may be regarded as two mutually dependent internal substitutions. If, as is generally conceded, the initial stage in substitution and rearrangement is the formation between the interacting molecules or groups of a residual linking, which subsequently establishes itself at the expense of another bond, then

Werner's theory of the Walden inversion [1] can be extended to all these cases: the application to the Beckmann rearrangement, regarded as a *trans*-interchange, would be

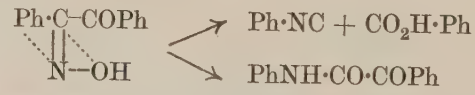


This view of the course of the Beckmann change, which was first advanced by H. Bucherer as early as 1914,[2] is therefore clearly consistent with other known phenomena relating to substitution, etc. If, however, it were found to apply generally, it would be necessary to reverse all configurations previously assigned to oximes on the basis of the Beckmann rearrangement.

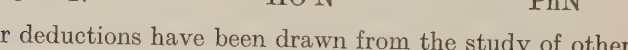
The first evidence in favour of reversal was advanced by J. Meisenheimer [3] in 1921, who showed that triphenyl*iso*oxazole on fission by the ozone method yielded the benzoyl derivative of β-benzilmonoxime, which must therefore be formulated as follows, although the opposite configuration had previously been assigned to this oxime on the basis of the Beckmann change:



It follows that the Beckmann rearrangement must involve *trans*-interchange thus:



Various observations have since been made tending to confirm this conclusion. Thus the oximes of *o*-chloro- and *o*-bromo-benzophenone, which by the Beckmann rearrangement yield anilides of the substituted benzoic acids, pass with ease into benz*iso*oxazoles [4]:



Similar deductions have been drawn from the study of other ortho-substituted aromatic ketones,[5] although the results are not in all cases conclusive.[6]

[1] A. Werner, *Ber.*, 1911, **44**, 881; *A.*, 1911, i, 424.

[2] "Lehrbuch der Farbenchemie," p. 202.

[3] *Ber.*, 1921, **54**, 3206; *A.*, 1922, i, 152. Compare *Ann. Report*, 1922, p. 8.

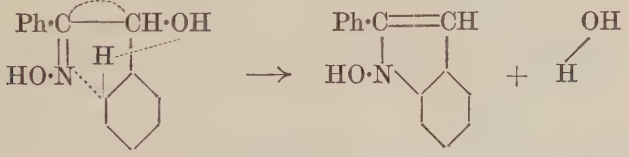
[4] J. Meisenheimer and H. Meis, *ibid.*, 1924, **57**, 289; *A.*, 1924, i, 433.

[5] K. von Auwers and O. Jordan, *ibid.*, p. 800; *A.*, 1924, i, 743; *ibid.*, 1925, **58**, 26; *A.*, i, 264; K. von Auwers, M. Lechner, and H. Bundesmann, *ibid.*, p. 36; *A.*, i, 265.

[6] Compare O. L. Brady and G. Bishop, *J.*, 1925, **127**, 1358.

The only case recorded in the literature in which the conversion of an oxime into a ring compound points to a configuration in harmony with the older conception of the Beckmann rearrangement is that of benzoin-α-oxime, which, according to E. Fischer and H. Hütz,[7] is converted into an indole derivative, whereas the β-oxime does not behave in this manner :

However, doubts about the constitution of the ring compound have been expressed by Fischer, and definite proof that it is not 2-phenylindoxyl is afforded by L. Kalb and J. Bayer's [8] synthesis of the latter, and its non-identity with the product obtained by Fischer and Hütz. The compound must therefore be 2-phenyl-1-hydroxyindole,[9] and its formation from an oxime of the opposite configuration to that depicted above can be explained, conformably with Robinson's theory of the Wagner transformation, by means of a six-membered partial valency cycle, involving (as in Bucherer's view of the Beckmann change) a partial linking between the benzene ring and the unoccupied side of the nitrogen atom :

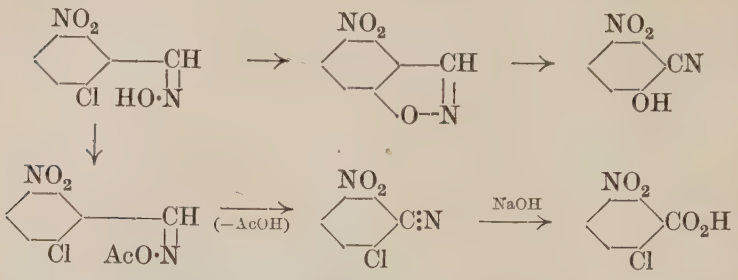


This case, therefore, falls into line with that view of the Beckmann change which involves transposing the configurations customarily assigned to ketoximes.

In the case of aldoximes, the question at issue is whether Hantzsch's assumption of the *cis*-elimination of acetic acid from the acetyl derivative is correct. Arguments in favour of *trans*-elimination have been adduced by E. Beckmann, O. Liesche, and E. Correns [10] and by K. von Auwers and B. Ottens,[11] but the most important evidence on the subject is that advanced by O. L. Brady and G. Bishop.[12] The two forms of 2-chloro-5-nitrobenzaldoxime were prepared and oriented by Hantzsch's method. It was then found that the oxime whose acetyl derivative lost acetic acid in this process readily underwent ring closure, yielding an *iso*oxazole

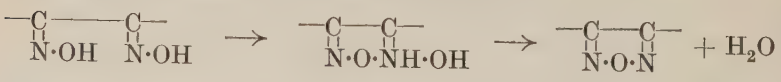
[7] *Ber.*, 1895, **28**, 585; *A.*, 1895, i, 371.
[8] *Ibid.*, 1912, **45**, 2150; *A.*, 1912, i, 727.
[9] J. Meisenheimer and H. Meis, *loc. cit.*
[10] *Ber.*, 1923, **56**, 341; *A.*, 1923, i, 228.
[11] *Ibid.*, 1924, **57**, 446; *A.*, 1924, i, 516.
[12] *J.*, 1925, **127**, 1357.

and ultimately a hydroxy-nitrile, under conditions in which the isomeric oxime remained largely unchanged :



Since ring formation would be expected to occur more readily when the hydroxyl group is vicinal to the halogenated phenyl group than when it is remote, this result indicates preferential *trans*-elimination of acetic acid in Hantzsch's orientation process, and a consequent reversal of the customary configurations of aldoximes.

These authors regard their experiments rather as a significant indication than a complete proof that the configuration of aldoximes should be inverted, and it would be desirable to maintain this reserve for the present both with regard to aldoximes and ketoximes, if only for the following reason. All the evidence in favour of inversion is based on the assumption that neighbouring groups interact most readily in ring closure, and are necessarily formed when a ring is broken. The first of these propositions is probably true in the great majority of cases; nevertheless it must be applied with caution, since the ready dehydration of *amphi*-glyoximes [13] shows that ring closure may, in certain circumstances, take place by a mechanism which obviates any necessity for the eliminated residues to be originally in close proximity : [14]



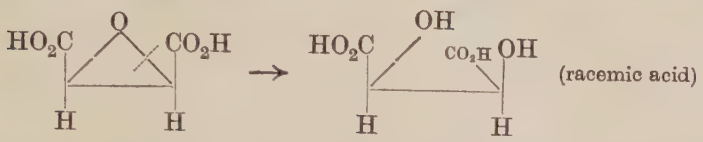
The second generalisation has been challenged by workers [15] who claim to have demonstrated "*trans*-ring fission," and although the instances described are obviously fissions involving Walden inversions (p. 105) affecting only the configurations of groups about

[13] J. Meisenheimer and W. Lamparter, *Ber.*, 1924, **57**, 276; *A.*, 1924, i, 432. J. Meisenheimer, H. Lange, and W. Lamparter, *Annalen*, 1925, **444**, 94; *A.*, i, 1073.

[14] Compare *Ann. Report*, 1924, p. 113, and O. L. Brady and G. Bishop, *loc. cit.*

[15] R. Kuhn and F. Ebel, *Ber.*, 1925, **58**, 919, 2088; *A.*, i, 780, 1378; J. Böeseken, *ibid.*, p. 1470; *A.*, i, 1237.

the separated atoms ("Sprengstücke"),[16] as, for instance, the hydrolysis of *cis*-ethyleneoxidedicarboxylic acid to racemic acid :[17]



(racemic acid)

there remain cases of so-called "resonance action" or "nascent activation" in which chemical reaction in one part of a molecule brings about some unexpected change in another.[18] Now this change may be a geometrical inversion. The formation of fumaric acid when copper maleate is decomposed with hydrogen sulphide is a case in point, for hydrogen sulphide has no action on maleic acid as such, either in the pure state or mixed with other copper salts.[19]

Thus, unlikely though it may seem, the possibility is not completely excluded that in Meisenheimer's experiment the fission by ozone of one double bond of the *iso*oxazole ring may give rise to inversion around the other, in which case the argument for inverting oxime configurations would collapse.

It may, however, truly be said that the work of Brady, Meisenheimer and their collaborators has established a strong *prima facie* case in favour of inversion, although further evidence is desirable before the matter can be regarded as conclusively settled.

In the above discussion the geometrical character of the isomerism met with in oximes is taken for granted—for reasons summarised in last year's Report. However, the complexity of oxime transformations is such that the Hantzsch–Werner geometrical conception must certainly be extended, as O. L. Brady and P. Dunn originally suggested,[20] by ascribing to each isomeride a tautomeric condition involving the appropriate nitrone form. The necessity

[16] J. Meisenheimer, *Ber.*, 1925, **58**, 1491; *A.*, i, 1335. Compare J. Böeseken, *loc. cit.*

[17] R. Kuhn and F. Ebel, *ibid.*, p. 919; *A.*, i, 780.

[18] R. Anschutz, *Annalen*, 1887, **239**, 161; *A.*, 1887, i, 916; K. von Auwers, *ibid.*, 1899, **309**, 316; *A.*, 1900, i, 84; H. Phillips, *J.*, 1923, **123**, 44; R. Stoermer and F. Bacher, *Ber.*, 1924, **57**, 15; *A.*, 1924, i, 400; P. Walden, *Ber.*, 1925, **58**, 237; *A.*, i, 349; R. Stoermer and P. K. Klockmann, *ibid.*, p. 1164; *A.*, i, 927; F. R. Goss and C. K. Ingold, *J.*, 1925, **127**, 2776.

[19] H. Skraup, *Monatsh.*, 1891, **12**, 108; *A.*, 1891, i, 1338. The analogous conversion of citraconic acid into mesaconic acid is described by R. Franz, *ibid.*, 1894, **15**, 209; *A.*, 1894, i, 403.

[20] *J.*, 1916, **109**, 659.

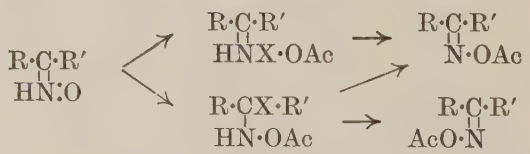
for some such extension has recently been emphasised,[21] and it has been pointed out that the nitrone forms would necessarily retain the distinctive geometrical configurations of the original isomeric oximes.[22] Thus it seems probable that in oxime chemistry, as in the chemistry of diazo-compounds, we encounter combined tautomerism and geometrical isomerism, complicated also, no doubt, by the ionisability of the individuals implicated.

Without discussion of the bearing of these various factors on oxime transformations in general, reference may be made to the interconversion of the geometrical isomerides. O. L. Brady and G. P. McHugh [23] have published a summary of the results obtained on acylating sixteen aldoximes with eight different acylating agents, and suggest that the changes of configuration observed are best accounted for by assuming the intervention of the nitrone form. Writing α for the configuration formerly regarded as *anti*, and β for the other one, the data may be tabulated as follows :

Reagent.	α-Oxime (9 examples).	β-Oxime (7 examples).
Acetic anhydride	α	β
Benzoyl chloride	α	α
Diphenylcarbamyl chloride	β	β
Ethyl chloroformate	α or β	(β) *
Chloro-2 : 4-dinitrobenzene	β	(—) †
Picryl chloride	β	(β) *
Phenylcarbimide	α and β	β
α-Naphthylcarbimide	α	β

* Indicated by isolation of nitrile. † Oxime group split off.

The explanation given, namely, that addition to the nitrone occurs in two ways, one of which may lead to an inversion of configuration,



corresponds closely with that offered by Brady and Dunn [24] to account for other inversions of oxime configurations, and has much to recommend it. In its results it is equivalent to ascribing a pseudo-basic character to the *iso*oxime structure : [25]

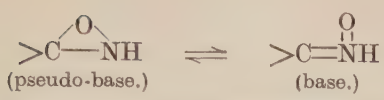
[21] J. P. Griffiths and C. K. Ingold, *J.*, 1925, **127**, 1698.

[22] In this connexion it is noteworthy that the complete set of four mono- and four di-oximes of *p*-methoxybenzil required by the geometrical theory has been described by J. Meisenheimer, H. Lange, and W. Lamparter, *loc. cit.*

[23] *J.*, 1925, **127**, 2414.

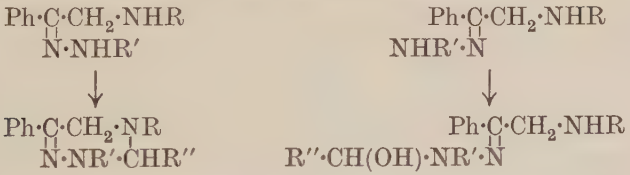
[24] *Loc. cit.*

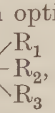
[25] *Ann. Report*, 1924, p. 113.



with consequent tautomerism in its salt-like additive products, and the possibility of geometrical inversion through the pseudo-salts :

Geometrical Isomerism of Hydrazones.—Pairs of stereoisomeric hydrazones have frequently been described, but no method of orientation in which any degree of confidence could be placed had until recently been evolved. M. Busch, G. Friedenberger, and W. Tischbein [26] have, however, described a series of hydrazones of ω-anilinoacetophenone which occur both in α (less fusible) and β (more fusible) forms. To these it seems possible to assign definite configurations, since the α-compounds combine with aldehydes, giving cyclic derivatives, whilst the β-isomerides yield open-chain aldehyde-ammonias and other complex substances :



Optically Active Sulphur Compounds.—The assumption that in oximes the hydroxyl group is bent out of the plane of the double linking attached to the tervalent nitrogen atom is now so familiar that the theoretical problems to which this conception gives rise, especially when it is considered in relation to the failure which has consistently attended efforts to obtain optically active, open-chain compounds of tervalent nitrogen,  , tend to be overlooked. It is therefore of great interest that instances of optical activity in which only three groups are attached to the central atom have been recorded.[27] The active compounds described are the ethyl and *n*-butyl esters of *p*-toluenesulphinic acid, $C_7H_7 \cdot SO \cdot OR$, which were obtained as $d + l$ mixtures, containing an excess of one enantiomorph, by digesting the *p*-toluensulphinate of an active alcohol (*l*-β-octanol) with ethyl or *n*-butyl alcohol; a partial interchange of alkyl radicals then took place in such a way as to favour

[26] *Ber.*, 1924, **57**, 1783; *A.*, 1925, i, 41.
[27] H. Phillips, *J.*, 1925, **127**, 2552.

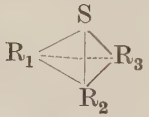
one of the active forms, somewhat as in asymmetric synthesis. This clearly shows that in these sulphinic esters the toluene group must be outside the plane formed by the sulphur atom and the two oxygen atoms of the sulphoxyl group, the central sulphur atom and its three attached groups occupying the corners of a tetrahedron.

This conclusion corresponds closely with the generally accepted interpretation of the optically active thionium salts described first by Sir W. J. Pope and S. J. Peachey,[28] and by S. Smiles.[29] Here, it is true, there are four groups attached to the central atom, but one of these is an ionisable acid radical which cannot materially influence the spatial arrangement of the non-dissociable complex (Werner). This complex must therefore be asymmetric itself, the four atoms in $\left[S\begin{smallmatrix}R_1\\R_2\\R_3\end{smallmatrix}\right]$ occupying the corners of a tetrahedron.[30] Thus the two classes of optically active sulphur compounds may both be referred to type I (below):

$\left[C_2H_5\cdot S<\begin{smallmatrix}CH_2\cdot CO_2H\\CH_3\end{smallmatrix}\right]X$ *Pope and Peachey* (1900).

$\left[O{=}S<\begin{smallmatrix}C_6H_4\cdot CH_3\\O\cdot C_2H_5\end{smallmatrix}\right]$ *Phillips* (1925).

Werner's principle that ionising linkings can be disregarded in considering stereochemical relationships enables a similar comparison to be made between optically resolvable ammonium salts and amine oxides; and since sulphoxides (to which sulphinic esters may be likened) can be regarded as internal thionium compounds, related to ordinary thionium salts as amine oxides are to ammonium salts, a correspondence of configuration would be expected in both cases. Thus we have two types (1 and 2) of spatial structure applicable to those optically active compounds of sulphur and nitrogen, respectively, which have been described up to the present time:



Type 1.

$\left[R_1{-}S<\begin{smallmatrix}R_2\\R_3\end{smallmatrix}\right]^+$ (*Thionium ion.*)

$\left[O{=}S<\begin{smallmatrix}R_1\\R_2\end{smallmatrix}\right]$ (*Sulphoxides.*)

Type 2.*

$\left[\begin{smallmatrix}R_1\\R_2\end{smallmatrix}\!>\!N\!<\!\begin{smallmatrix}R_3\\R_4\end{smallmatrix}\right]^+$ (*Ammonium ion.*)

$\left[\begin{smallmatrix}R_1\\R_2\end{smallmatrix}\!>\!N\!<\!\begin{smallmatrix}R_3\\O\end{smallmatrix}\right]$ (*Amine oxides.*)

[28] *J.*, 1900, **77**, 1072. [29] *Ibid.*, p. 1174.

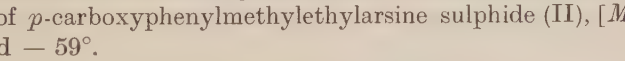
[30] A. Werner, "Lehrbuch der Stereochemie," p. 317 (1904).

* Any doubt which might have existed with regard to this structure is removed by the recent investigation by W. H. Mills and E. H. Warren (*J.*, 1925, **127**, 2507).

Phillips's paper contains an interesting discussion of the possible reasons for the fact that the sulphur atom does not occupy the most central position with respect to R_1, R_2, and R_3 in type 1. The obvious suggestion, to which the octet theory leads, that the place of R_4 in type 2 is taken in type 1 by a " lone pair " of electrons (A), is negatived partly on the ground of the non-asymmetric character [31] of the tervalent nitrogen atom in $NR_1R_2R_3$, where there would similarly be a " lone pair " of electrons (B) :

The conclusion drawn is that the positive charge associated with the sulphur atom both in thionium salts and in sulphinic esters is—apart from the attachment of three dissimilar groups—the essential condition of asymmetry.

Optically Active Arsenic Compounds.—Despite the probable similarity between the stereochemical configurations of compounds of quinquevalent arsenic and those of corresponding derivatives of nitrogen and phosphorus, attempts to resolve arsonium compounds until recently met with little success, although G. J. Burrows and E. E. Turner [32] obtained a solution of phenyl-α-naphthylbenzylmethylarsonium iodide (I) which showed a feeble dextrorotation. A much more satisfactory case is now recorded by W. H. Mills and R. Raper,[33] who have obtained optically pure enantiomorphous modifications of *p*-carboxyphenylmethylethylarsine sulphide (II), $[M]^{20°}_{5461}$ + 60° and − 59°.



The compound (II) is constituted similarly to the amine and phosphine oxides resolved by J. Meisenheimer, but whereas the latter substances are basic, forming salts of the types $[R_1R_2R_3N(OH)]X$ and $[R_1R_2R_3P(OH)]X$, the tertiary arsenic sulphides, $R_1R_2R_3As{:}S$, are chemically indifferent, and the compound (II) derives its salt-forming properties from the carboxyl group. Thus the arsenic atom is left, as far as possible, undisturbed by the processes of salt formation and decomposition necessary to the resolution, and this fact may have contributed to its success.

Mechanism of Isomeric Change.

So many views have been expressed with regard to the mechanism of tautomeric and isomeric changes that consider-

[31] J. Meisenheimer and M. Schütze, *Ber.*, 1923, **56**, 1353; *A.*, 1923, i, 839.
[32] *J.*, 1921, **119**, 426. [33] *Ibid.*, 1925, **127**, 2479.

able interest attaches to cases suitable for detailed and quantitative study. An important investigation on this subject has been published during the year by A. W. Chapman,[34] who has examined in some detail a case of the migration of a group in the amido-imidol triad system :

It has frequently been suggested that in changes of this kind the migration of the mobile atom or group is preceded by its dissociation from the remainder of the molecule, which then undergoes valency-rearrangement and, by subsequent recombination, produces the isomeric compound. The absence of by-products formed by the combination of two similar radicals is then accounted for by regarding the dissociation as ionic in character, in conformity with the conception which assumes antecedent ion-formation in all organic reactions. The view that isomeric change occurs only subsequently to ionisation has recently been applied to rearrangements in the camphene series.[35]

On the other hand, it has been held that such transformations are entirely internal in character, and occur through the operation of partial valencies inside the system, without the intervention of ions.

In common with other *O*-substituted derivatives of amides, *N*-phenylbenziminophenyl ether undergoes isomeric change on heating, the substituent attached to oxygen becoming transferred to the nitrogen atom of the amide group :

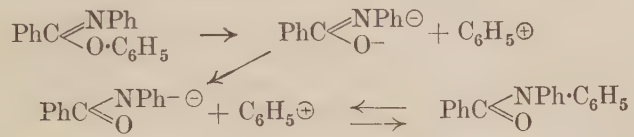
The reaction appears to be peculiarly well adapted to quantitative investigation, as it proceeds without the formation of any by-product, and is not measurably reversible under the conditions used. A dynamical study showed that it was strictly monomolecular.

In order to test the validity of the ionic mechanism, the electrical conductivity of the material was measured during the isomerisation. At all stages the conductivity was small, but, as the reaction progressed, it increased from the value given by the pure

[34] *J.*, 1925, **127**, 1992.

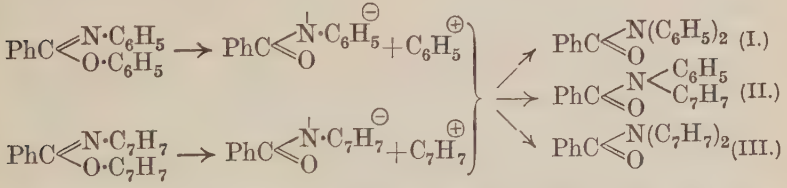
[35] H. Meerwein and K. van Emster, *Ber.*, 1922, **55**, 2500; *A.*, 1922, ii, 751; H. Meerwein and R. Wortmann, *Annalen*, 1924, **435**, 190; *A.*, 1924, i, 188; H. Meerwein and F. Monforte, *ibid.*, p. 207; *A.*, 1924, i, 191; *Ann. Report*, 1924, p. 96.

imino-ether to a final steady value, which was identical, within the limits of experimental error, with that characteristic of the carefully purified amide. This proved conclusively that ions were present throughout the change, which might therefore be explained in terms of the ionic mechanism in the following manner :



provided that appropriate assumptions with regard to the relative velocities of the component changes were made to account for the monomolecular character of the complete reaction.

It therefore remained to ascertain whether these ions are really responsible for the transformation, and for this purpose the fact was utilised that *N*-*p*-tolylbenzimino-*p*-tolyl ether undergoes rearrangement at the same temperatures as *N*-phenylbenzimino-phenyl ether. If the change is ionic in one case, it should be so in the other, and a mixture of the two imino-ethers should give rise to ions which on recombination would yield, not only the two symmetrical products (I and III), but also the phenyl-*p*-tolyl-compound (II) :

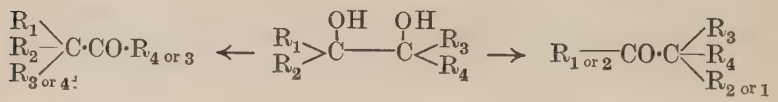


No such interchange of groups occurred, each rearrangement proceeding independently of the other. It is, therefore, clear that the isomeric change of imino-ethers into substituted amides does not involve prior fission into ions, but is a purely internal process. Since this inference can probably be extended to other similar molecular rearrangements, the conclusion may be drawn that the ionic hypothesis is not generally applicable to such changes, although it may constitute a facilitating mechanism in certain cases.[36]

Migratory Tendencies of Different Groups.—Numerous papers have been published within recent years on the relative migratory tendencies of different groups in the rearrangements which often accompany the dehydration of α-glycols. It appears, however, that the controlling conditions are somewhat complex. In the

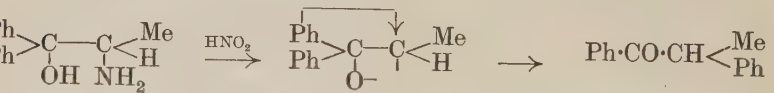
[36] *Ann. Report*, 1924, p. 98.

general case migration can obviously occur from either of the hydroxyl-bearing carbon atoms to the other :



and a variety of carbonyl compounds may be formed, in addition to ethylene oxides—complicating factors which greatly increase the difficulty of comparison. It appears, for instance, that in the dehydration of α-naphthylhydrobenzoin all the possible products are formed simultaneously.[37]

A considerable simplification of method seems to have been provided by the discovery, by McKenzie and his collaborators, of the " semipinacolinic deamination " of amino-alcohols by means of nitrous acid,[38] since in this change migration occurs always away from the hydroxyl-bearing carbon, as in the following case : [39]



Moreover the reaction does not appear prone to yield ethylene oxides,[40] as was formerly supposed.[41] If, therefore, two different radicals are attached to the carbon atom bearing the hydroxyl group, a decision with regard to their relative tendencies towards migration can be obtained. In this way the following comparisons have been made : (*a*) *p*-anisyl > phenyl [42] (which agrees with conclusions based on the more complex glycol dehydrations) ; [43] (*b*) phenyl > α-naphthyl (glycol dehydrations had led to inconclusive results) ; [44] (*c*) phenyl > methyl.[45] It is to be hoped that

[37] A. McKenzie and W. S. Dennler, *J.*, 1924, **125**, 2105 ; A. McKenzie and R. Roger, *ibid.*, p. 844 ; A. Orékhov and M. Tiffeneau, *Compt. rend.*, 1924, **178**, 1619 ; *A.*, 1924, i, 729.

[38] A. McKenzie and A. C. Richardson, *J.*, 1923, **123**, 79 ; A. McKenzie and W. S. Dennler, *loc. cit.* ; A. McKenzie and R. Roger, *loc. cit.* ; A. McKenzie and G. O. Wills, *J.*, 1925, **127**, 283.

[39] A. McKenzie and G. O. Wills, *loc. cit.* Compare F. Bettzieche, *Z. physiol. Chem.*, 1924, **140**, 273 ; *A.*, 1925, i, 251.

[40] A. Orékhov and M. Roger, *Compt. rend.*, 1925, **180**, 70 ; *A.*, i, 261.

[41] C. Paal and E. Weidenkaff, *Ber.*, 1905, **38**, 1686 ; 1906, **39**, 2062 ; *A.*, 1905, i, 436 ; 1906, i, 583.

[42] A. Orékhov and M. Roger, *loc. cit.*

[43] M. Tiffeneau and A. Orékhov, *Bull. Soc. chim.*, 1925, (iv), **37**, 430 ; *A.*, i, 679.

[44] A. McKenzie and W. S. Dennler, *loc. cit.* ; A. Orékhov and M. Tiffeneau, *loc. cit.*

[45] A. McKenzie and A. C. Richardson, *loc. cit.* ; A. McKenzie and R. Roger, *loc. cit.*

further comparisons of this kind will be made, as the results cannot fail to be of importance in relation to the theory of affinity distribution and its effect in facilitating isomeric change.

With regard to the mechanism of these deaminations, it is clear that they take place without the intermediate formation of glycols or ethylene oxides.[46] The explanations that have been suggested have been based on the conception of intermediate free radicals, as indicated by the preceding formulæ. On the other hand, ethylene oxides are known to undergo the corresponding rearrangements, although at higher temperatures.[47] It seems probable that elimination of nitrogen from a cyclic diazo-oxide may fulfil the same part in promoting the semipinacolinic deamination as the elimination of water does in the Wagner rearrangement, the mechanism of which was discussed in last year's Report.

Auto-oxidation and the Structure of Ozonides.

It has long been known that when an unsaturated substance is oxidised by atmospheric oxygen in the presence of another compound incapable, under ordinary circumstances, of auto-oxidation, the latter also is sometimes oxidised. This phenomenon was at one time described as the "activation" of oxygen, and was regarded as a consequence of the formation either of ozone or of hydrogen peroxide.

It was shown, however, by Engler and others [48] that the oxidising agent produced during auto-oxidation is neither ozone nor hydrogen peroxide but a compound with oxygen of the unsaturated substance itself. In the case of pinene, for instance, the activity of the auto-oxidation product is retained for years if the material is kept in the dark, and the active constituent remains in the residue when much of the unchanged pinene is removed by distillation. The reactions of the active material, moreover, are not those of ozone or hydrogen peroxide, but those of an organic peroxide.

In most cases these peroxide-like substances are very difficult to purify, but analysis indicates that the number of added oxygen atoms is two,[49] or some multiple of two if auto-oxidation takes place at more than one point in the molecule. In the case of dimethylfulvene a definite dioxide has been isolated.[50]

[46] A. Orékhov and M. Roger, *loc. cit.*

[47] M. Tiffeneau, A. Orékhov, and J. Lévy, *Compt. rend.*, 1924, **179**, 977; *A.*, 1925, i, 544; J. Lévy and R. Lagrave, *ibid.*, 1925, **180**, 1032; *A.*, i, 679.

[48] C. Engler and W. Wild, *Ber.*, 1897, **30**, 1669; *A.*, 1897, ii, 402; C. Engler and J. Weissberg, *ibid.*, 1898, **31**, 3046; *A.*, 1899, i, 221.

[49] C. Engler, *ibid.*, 1900, **33**, 1090, 1097, 1109; *A.*, 1900, i, 399 *et seq.*

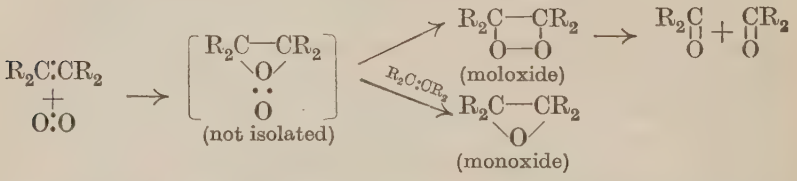
[50] C. Engler and W. Frankenstein, *ibid.*, 1901, **34**, 2933; *A.*, 1901, i, 657.

These facts, and many others,[51] are consistent with the Engler–Bach theory that the first stage of auto-oxidation consists in the addition of molecular oxygen to give a "moloxide" (XO_2), which may either oxidise more of the original substance to the monoxide (XO), or oxidise some other substance (if present) even although this may not be auto-oxidisable in the ordinary sense:

$$\begin{cases} X + O_2 = XO_2 \text{ (first stage)} \\ XO_2 + X = 2XO \text{ (second stage)} \\ XO_2 + A = XO + AO \text{ ("activation" effect).} \end{cases}$$

In some cases the action can be arrested at the first stage; in others the products from both stages are found; again in others [52] the second stage follows very rapidly upon the first.

These conceptions have been developed to a considerable extent by H. Staudinger,[53] who formulates the auto-oxidation of ethylene derivatives thus:



The scheme is illustrated by reference to the ketens and other ethylenic compounds.

The keto-ketens are readily auto-oxidisable, the sensitivity towards atmospheric oxygen of diphenylketen being comparable with that of triphenylmethyl.[54]

In general, the primary auto-oxidation products of ketens are their moloxides, which are precipitated as polymerides when oxygen is passed into an ethereal solution of the keten at temperatures below $-20°$.[55] Dimethylketen dioxide, the most stable of the series, is thus obtained as an amorphous powder which is violently explosive. In ethereal suspension at the ordinary temperature decomposition takes place without explosion, giving acetone and carbon dioxide, a reaction comparable with the well-known division of β-lactones.

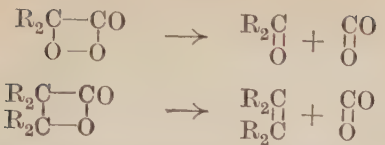
[51] A. Klages and S. Heilmann, *Ber.*, 1904, **37**, 1449; *A.*, 1904, i, 487; M. Tiffeneau, *Bull. Soc. chim.*, 1902, [iii], **27**, 1066; *A.*, 1903, i, 81; O. Wallach, *Annalen*, 1905, **343**, 28; *A.*, 1906, i, 194; G. Ciamician and P. Silber, *Ber.*, 1903, **36**, 4266; *A.*, 1904, i, 161.

[52] *Ann. Report*, 1924, p. 109.

[53] *Ber.*, 1925, **58**, 1075; *A.*, i, 898.

[54] H. Staudinger, "Die Ketene," p. 49.

[55] H. Staudinger, K. Dyckerhoff, H. W. Klever, and L. Ruzicka, *Ber.*, 1925, **58**, 1079; *A.*, i, 933.



Diethylketen moloxide is less stable, and undergoes a similar decomposition into diethyl ketone and carbon dioxide. Phenylmethylketen moloxide is still less stable, and must be prepared at — 80°, since at higher temperatures it passes into acetophenone and carbon dioxide. Diphenylketen moloxide is unstable even at — 80°.

The peroxidic character of these substances is shown by their explosiveness, and by the fact that they readily oxidise potassium iodide solution. On the other hand, no loss of oxygen to give monoxides (see below) takes place on thermal decomposition.

When oxygen is passed into keten solutions at the ordinary temperature the moloxide is not obtained, but two types of "secondary" oxidation products are formed, namely, (*a*) ketones and carbon dioxide,

$$R_2C{:}CO + O_2 \longrightarrow R_2CO + CO_2,$$

(*b*) keten monoxides, which, like the dioxides, are obtained in polymerised forms, although their reactions can be most simply represented by means of the monomolecular formula, $R_2C{-}{-}CO$ (O).

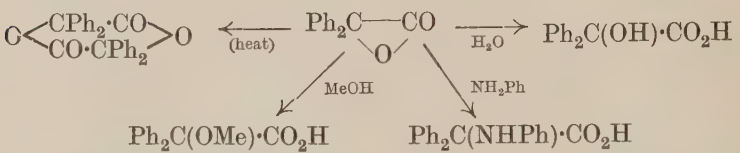
The following table shows how the relative proportion of ketone and carbon dioxide, obtained by auto-oxidation at the ordinary temperature, varies with the stability of the moloxide prepared at low temperatures :

Keten.	Stability of moloxide.	Products of auto-oxidation at the ordinary temperature. (*a*) Ketone+carbon dioxide.	(*b*) Keten monoxide.
$Me_2C{:}CO$	Stable at −10°	About 85%	None obtained
$Et_2C{:}CO$	Rather less stable	,, 60%	Small quantity
$MePhC{:}CO$	Stable at −80°	,, 30%	Larger quantity
$Ph_2C{:}CO$	Unstable at −80°	,, 15%	Main product

Since the quantity of ketone and carbon dioxide increases with increasing stability of the keten moloxide, it is concluded that they are formed by the decomposition (thermal division) of the latter. The variation in the quantity of keten monoxide produced shows that it cannot be derived from the same proximate source as the ketone and carbon dioxide, and for this reason the monoxide is regarded as arising from some earlier oxygen-addition product than the oxide from which the ketone and carbon dioxide are formed. These conclusions, which are consistent with the properties of the

moloxides, are expressed in the general scheme of auto-oxidation given above.

Diphenylketen monoxide, although polymerised, behaves in many ways as the α-lactone of benzilic acid. The direction of addition of methyl alcohol and aniline is curious, the products being α-methoxydiphenylacetic acid and α-anilinodiphenylacetic acid, respectively, unaccompanied by the expected ester or anilide of benzilic acid.



Diphenylethylene [56] yields a moloxide which is highly polymerised and singularly stable; on heating, however, it breaks down into benzophenone and formaldehyde :

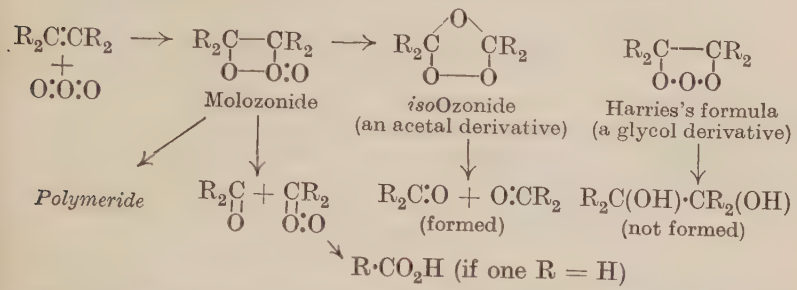
In this reaction depolymerisation to the labile monomolecular oxide doubtless precedes division into the carbonyl compounds, since the production of benzophenone and formaldehyde during the auto-oxidation of diphenylethylene cannot be attributed to the decomposition of polymerised moloxide, which is stable unless heated.

Ozonides.—By analogy with the mechanism of auto-oxidation it is suggested [57] that the first step in the reaction between ozone and an unsaturated substance is the formation of a " molozonide," corresponding in structure with a moloxide. The molozonide may either polymerise (just as the moloxides do), giving ozonides of high molecular weight, such as are obtained from *cyclo*pentene and *cyclo*hexene, or it may isomerise to an " *iso*ozonide," to which class the stable, distillable ozonides, like ethylene ozonide, are assumed to belong, or it may undergo thermal division to give a ketone and a ketone peroxide or acid.

This view possesses clear advantages over most older views regarding the structure of ozonides. If, for instance, the *iso*-ozonide formula is compared with Harries's ozonide formula, it is seen that the first is similar in certain respects to an acetal, whilst the second represents a glycol peroxide. The latter on reduction

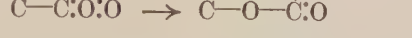
[56] H. Staudinger, *Ber.*, 1925, **58**, 1075; *A.*, i, 898.
[57] *Idem, ibid.*, p. 1088; A., i, 898.

ought, therefore, to give a glycol, whereas the former would be expected to give the ketonic products actually obtained.



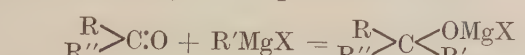
It is noteworthy that the tendency to polymerisation is most marked in those cases in which conversion into an *iso*ozonide might be expected to occur with unusual difficulty owing to the occurrence of the original double linking in a ring structure. Further, the presence of acetic acid appears to facilitate isomeric change, whereas solvents which tend to favour association cause, in many cases, the formation of highly polymerised substances.

The rupture of the carbon chain which, according to this view, takes place when the molozonide undergoes rearrangement may be compared with the change which occurs when ketone peroxides pass into esters : [58]



Mechanism of the Grignard Reaction.

Since the classic investigations of P. Barbier and V. Grignard [59] the addition between a magnesium alkyl halide and a carbonyl compound has usually been represented thus :



the addition product (I) being a halogenomagnesium alkyloxide.

Within recent years, however, dissatisfaction with this view has been expressed, and alternatives have been suggested. J. von Braun and G. Kirschbaum [60] proposed an oxonium structure (II) for the addition compound, and J. Meisenheimer and J. Casper [61] advanced a "co-ordination formula" (III) with magnesium as the central atom. In order to make the co-ordination number equal

[58] A. v. Baeyer and V. Villiger, *Ber.*, 1899, **32**, 3625; 1900, **33**, 858; *A.*, 1900, i, 133, 328.

[59] *Compt. rend.*, 1899, **128**, 111; *A.*, 1899, i, 323; *ibid.*, 1900, **130**, 1323; *A.*, 1900, i, 382; and later papers.

[60] *Ber.*, 1919, **52**, 1725; *A.*, 1920, i, 30.

[61] *Ibid.*, 1921, **54**, 1655; *A.*, 1921, i, 654.

to 4, a molecule of ether was included in the complex, but since the ether-content of Grignard addition compounds prepared in that solvent varies both with the nature of the magnesium alkyl halide and with the carbonyl compound in a manner which is not fully understood, it is simpler to consider the ether-free substances which, as is well known, can be isolated in the solid form. Leaving the ether out of formula (III) would, according to H. Rheinboldt and H. Roleff,[62] give to the magnesium atom the co-ordination number 3.

(II.) $\begin{matrix} R \\ R'' \end{matrix}\!\!>\!C\!:\!O\!<\!\!\begin{matrix} MgX \\ R' \end{matrix}$ $\qquad\qquad$ $\begin{matrix} RR''CO \\ Et_2O \end{matrix}\!\!>\!Mg\!<\!\!\begin{matrix} X \\ R' \end{matrix}$ (III.)

Despite these various counter-suggestions, no clear demonstration had been given of the necessity for abandoning the previously accepted view, until Rheinboldt and Roleff ingeniously took advantage of the observation made by K. Hess and H. Rheinboldt [63] that Grignard addition compounds may decompose on heating with the elimination of an olefin and the formation, after addition of water, of a reduction product :

$$[RR'C\!:\!O + MgBr\cdot C_2H_5] \xrightarrow[H_2O]{} RR'CH\cdot OH + C_2H_4.$$

It is evident that the normal Grignard reaction between RR″C:O and R′MgX, leading to RR′R″C·OH, yields no evidence of any lack of equivalence between R, R′, and R″ in the initial addition compound, since all these groups are similarly situated in the final product. On the other hand, the side-reaction observed by Hess and Rheinboldt marks off one of these groups from the other two, and can be used to test their equivalence in the compound undergoing this decomposition. If, for instance, these compounds be of the type represented by formula (I), then the addition products from

$$\begin{matrix} C_6H_5 \\ R \end{matrix}\!\!>\!C\!:\!O + Mg\!<\!\!\begin{matrix} R' \\ X \end{matrix} \text{ and from } \begin{matrix} C_6H_5 \\ R' \end{matrix}\!\!>\!C\!:\!O + Mg\!<\!\!\begin{matrix} R \\ X \end{matrix}$$

should be identical, and the subsequent course of the reaction should be the same in each case; that is to say, the same by-products should be obtained, as well as the normal carbinol.

This was tested [64] in cases in which R′ was a radical, like *iso*-butyl, capable of being eliminated as an olefin, and it was found that whereas benzaldehyde and magnesium *iso*butyl bromide gave, in addition to the expected secondary alcohol, a large yield of benzyl alcohol, *iso*butylene being eliminated,

$$\begin{matrix} C_6H_5 \\ H \end{matrix}\!\!>\!C\!:\!O + MgBr\cdot C_4H_9 \xrightarrow[H_2O]{} \begin{cases} C_6H_5\cdot CH(OH)\cdot C_4H_9 \\ C_6H_5\cdot CH_2\cdot OH + C_4H_8, \end{cases}$$

[62] *Ber.*, 1924, **57**, 1921; *A.*, 1925, i, 6.

[63] *Ibid.*, 1921, **54**, 2043; *A.*, 1921, i, 777. Compare P. Schorigin, *Ber.*, 1908, **41**, 2717; *A.*, 1908, i, 881.

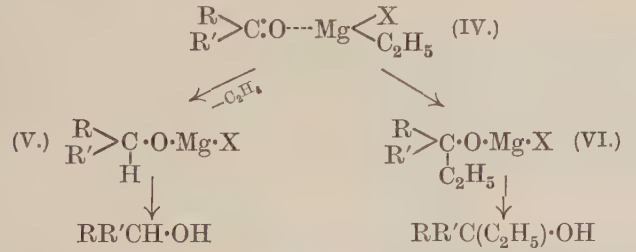
[64] *Ibid.*, 1924, **57**, 1921; *A.*, 1925, i, 6.

only the secondary alcohol was obtained when *iso*valeraldehyde and magnesium phenyl bromide were employed :

$$\begin{matrix} C_4H_9 \\ H \end{matrix}\!\!>\!C\!:\!O + MgBr\cdot C_6H_5 \longrightarrow C_6H_5\cdot CH(OH)\cdot C_4H_9.$$

Further, the bromomagnesium alcoholate, $C_6H_5\cdot CH(OMgBr)\cdot C_4H_9$, corresponding in constitution to formula (I), was prepared directly from phenyl*iso*butylcarbinol and was found to give no *iso*butylene on heating, and no benzyl alcohol on subsequent treatment with water, the original carbinol alone being recovered.

From these and similar results, Rheinboldt and Roleff conclude that the initial addition products of magnesium alkyl halides with carbonyl compounds cannot have a constitution in which the alkyl group introduced with magnesium is equivalent in position to the others, and, following Hess and Rheinboldt, they suggest formula (IV). Some such structure may well account for the elimination of the olefin, but, as J. Meisenheimer [65] points out, it is difficult to explain the normal reaction on the basis of this formula alone. It is therefore assumed that the original addition compound may undergo rearrangement to a halogenomagnesium alkyloxide either with or without the elimination of an olefin (V and VI) :



The scheme given is Meisenheimer's; Rheinboldt and Roleff adopt a slightly different interpretation of the elimination of the olefin, but in other respects their conclusions are closely similar.

The Metallic Ketyls.

This field of investigation, opened up by W. Schlenk and T. Weickel in 1911, has been further explored during the past two years by Blicke and his collaborators, who have published detailed investigations of the action of sodium on benzaldehyde and a number of benzoic esters.

Schlenk and Weickel [66] concluded that the coloured reactive compounds obtained previously by E. Beckmann and T. Paul [67] by the

[65] *Annalen*, 1925, **442**, 180; *A.*, i, 527.
[66] *Ber.*, 1911, **44**, 1182; *A.*, 1911, i, 545.
[67] *Annalen*, 1888, **266**, 1; *A.*, 1889, 78.

action of sodium on benzaldehyde, benzophenone, and various other aromatic ketones were not, strictly speaking, the sodio-derivatives of glycols,

$$2R_2C{:}O + 2Na \longrightarrow \begin{matrix} R_2C{\cdot}ONa \\ | \\ R_2C{\cdot}ONa' \end{matrix}$$

but were tervalent carbon compounds, to which the name " ketyl " was given :

$$R_2C{:}O + Na \longrightarrow R_2\dot{C}{\cdot}ONa.$$

The evidence in favour of the ketyl structure was originally purely chemical, being based, for instance, on the reactions with oxygen, iodine, and methyl iodide :

$$2R_2\dot{C}{\cdot}ONa + O_2 \longrightarrow \begin{matrix} R_2C{\cdot}O{\cdot}O{\cdot}CR_2 \\ | \quad\quad | \\ ONa \quad ONa \end{matrix} \longrightarrow 2R_2C{:}O + 2NaO.$$

$$2R_2\dot{C}{\cdot}ONa + I_2 \longrightarrow \begin{matrix} 2R_2CI \\ | \\ ONa \end{matrix} \longrightarrow R_2C{:}O + NaI.$$

$$2R_2\dot{C}{\cdot}ONa + CH_3I \longrightarrow \begin{cases} R_2C(CH_3){\cdot}ONa \xrightarrow{H_2O} R_2C(CH_3){\cdot}OH \\ + \\ R_2CI{\cdot}ONa \longrightarrow R_2C{:}O + NaI \end{cases}.$$

Later [68] it was shown that the soluble sodium compound of phenyl *p*-diphenylyl ketone had a molecular weight closely corresponding with the tervalent carbon formula, but, in order to account for the circumstance that on treatment with water not only the alcohol and ketone, but also the corresponding pinacol, may be produced, an equilibrium with the bimolecular form was assumed :

$$R_2C{:}O + Na \longrightarrow \begin{matrix} R_2C{\cdot}ONa \\ | \\ R_2\dot{C}{\cdot}ONa \end{matrix} \xrightarrow{H_2O} \begin{matrix} R_2C{\cdot}OH \\ | \\ R_2\dot{C}{\cdot}OH \end{matrix}$$

$$\Downarrow\Uparrow$$

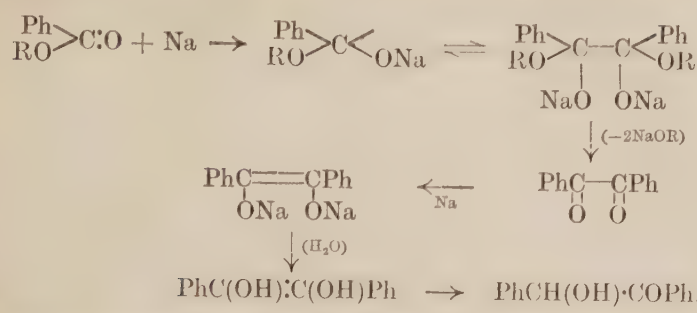
$$2R_2\dot{C}{\cdot}ONa \xrightarrow{H_2O} 2R_2\dot{C}{\cdot}OH \longrightarrow \begin{cases} R_2CO \\ + \\ R_2CH{\cdot}OH. \end{cases}$$

This is also in agreement with the fact that the same sodium compound can be obtained from the ketone and from the pinacol by the action of sodium.[69]

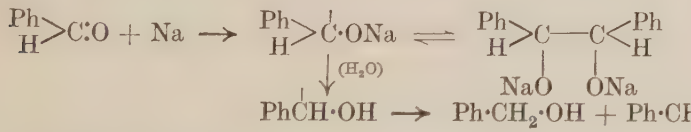
The action of sodium on benzoic esters [70] appears to be similar to the above, but the bimolecular sodium compounds, which can be regarded as derived from di-alcoholates of benzil, spontaneously lose two molecules of sodium alkyloxide, yielding benzil, which may be converted by the further action of sodium into the disodio-compound

[68] W. Schlenk and A. Thal, *Ber.*, 1913, **46**, 2840; *A.*, 1913, i, 1205.
[69] S. F. Acree, *Amer. Chem. J.*, 1903, **29**, 588; *A.*, 1903, i, 724.
[70] F. F. Blicke, *J. Amer. Chem. Soc.*, 1925, **47**, 229; *A.*, i, 662.

of stilbenediol.[71] The latter on treatment with water yields benzoin : [72]



Similar changes occur in the reaction between sodium and benzaldehyde. When one atomic proportion of sodium is used in ethereal solution, the metal dissolves and a coloured solution is formed, from which the ketyl separates as a deep green precipitate On addition of water and acid, the green colour is immediately discharged and a solution is obtained containing benzyl alcohol, benzaldehyde, benzoic acid, benzyl ether, benzyl benzoate, and benzoin.[73] The first two of these substances are, apparently, the normal products of the action of water upon the ketyl. The ketyl reduces benzaldehyde to benzyl alcohol and is itself transformed into sodium stilbenediol, which is ultimately converted into benzoin in the manner shown above. The benzyl benzoate is probably formed by the action of sodium benzyloxide on benzaldehyde,[74] in which reaction benzyl ether is known to appear as a by-product.[75] The benzyl benzoate may also give rise to sodium stilbenediol and thence to benzoin :



It is noteworthy that the products obtained from benzaldehyde appear to arise mainly from the monomolecular ketyl, whereas in the case of benzoic esters the bimolecular compound seems to be the principal source of the products obtained.

[71] H. Staudinger and A. Binkert, *Helv. Chim. Acta*, 1922, **5**, 705; *A.*, 1922, i, 1016; A. Scheuing and A. Hensle, *Annalen*, 1924, **440**, 172; *A.*, 1925, i, 27.

[72] A. Lachman, *J. Amer. Chem. Soc.*, 1924, **46**, 708; *A.*, 1924, i, 649.

[73] F. F. Blicke, *ibid.*, 2560; *A.*, 1925, i, 37.

[74] L. Claisen, *Ber.*, 1887, **20**, 646; *A.*, 1887, 574; C. A. Kohn and W Trantom, *J.*, 1899, **75**, 1161.

[75] O. Kamm and W. F. Kamm, *J. Amer. Pharm. Assoc.*, 1922, **11**, 599.

An interesting property of the sodium ketyls, which appears to be general, is their power to combine with another atom of sodium, giving a disodio-compound in which the metallic atom combined with carbon is extremely reactive : [76]

$$(C_6H_5)_2C{:}O \longrightarrow (C_6H_5)_2\overset{|}{C}{\cdot}ONa \longrightarrow (C_6H_5)_2CNa{\cdot}ONa.$$

Thus the disodio-compound derived from benzophenone readily combines with carbon dioxide or bromobenzene, yielding, after treatment with water, benzilic acid and triphenylcarbinol, respectively. This, no doubt, is the explanation of H. Frey's observation that benzophenone, bromobenzene (1 mol.), and sodium (2 mols.) react to give an almost quantitative yield of triphenylcarbinol.[77] The same end-product is obtained when benzoic esters are treated with bromobenzene and an excess of sodium,[78] and a similar explanation can be given :

$$\begin{matrix} Ph \\ RO \end{matrix}\!\!>\!C{:}O \xrightarrow[(2Na)]{} \begin{matrix} Ph \\ RO \end{matrix}\!\!>\!CNa{\cdot}ONa \xrightarrow[(+PhBr)]{} Ph_2C\!<\!\begin{matrix} ONa \\ OR \end{matrix} \xrightarrow[(-NaOR)]{} Ph_2C{:}O$$
$$\xrightarrow[(2Na)]{} Ph_2CNa{\cdot}ONa \xrightarrow[(PhBr)]{} Ph_3C{\cdot}ONa \xrightarrow[(H_2O)]{} Ph_3C{\cdot}OH.$$

Derivatives of cyclo*Propane and* cyclo*Butane.*

Formation by Malonic Ester Synthesis.—Attention has often been directed to the remarkable influence of substituents on ring closure. For example, the condensation of ethyl sodiomalonate with trimethylene dibromide leads to a *cyclo*butane ester,[79]

$$CH_2\!<\!\begin{matrix} CH_2Br \\ CH_2Br \end{matrix} + 2CHNa(CO_2Et)_2 \longrightarrow CH_2\!<\!\begin{matrix} CH_2 \\ CH_2 \end{matrix}\!\!>\!C(CO_2Et)_2,$$

whereas condensation with ethyl $\alpha\alpha'$-dibromo-$\beta\beta$-dimethylglutarate [80] yields, not the analogous *cyclo*butane derivative, but an isomeric *cyclo*propane compound :

$$CMe_2\!<\!\begin{matrix} CHBr{\cdot}CO_2R \\ CHBr{\cdot}CO_2R \end{matrix} + 2CHNa(CO_2R)_2 \longrightarrow$$
$$CMe_2\!<\!\begin{matrix} CH{\cdot}CO_2R \\ C(CO_2R){\cdot}CH(CO_2R)_2 \end{matrix}.$$

Two causes might be suggested to account for this difference.

[76] W. Schlenk, J. Appenrodt, A. Michael, and A. Thal, *Ber.*, 1914, **47**, 486; *A.*, 1914, i, 396; F. F. Blicke, *loc. cit.*

[77] *Ber.*, 1895, **28**, 2520; *A.*, 1896, i, 99.

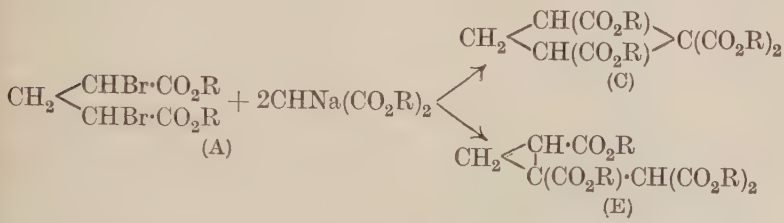
[78] P. Schorigin, *Ber.*, 1907, **40**, 3115; *A.*, 1907, i, 753; F. F. Blicke, *J. Amer. Chem. Soc.*, 1925, **47**, 229; *A.*, i, 662.

[79] W. H. Perkin, jun., *J.*, 1887, **51**, 4.

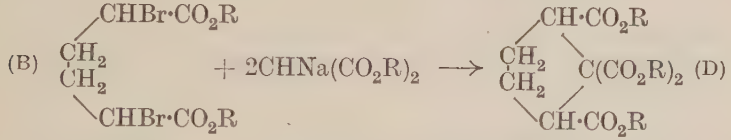
[80] W. H. Perkin, jun., and J. F. Thorpe, *J.*, 1901, **79**, 729. Compare C. K. Ingold and J. F. Thorpe, *ibid.*, 1919, **115**, 320.

First, the effect of the carbethoxyl groups in increasing the reactivity of the adjacent carbon atoms might favour their direct union by elimination of hydrogen bromide. Secondly, substitution of the *gem*-dimethyl group would be expected to augment the stability of the *cyclo*propane compound relatively to that of its *cyclo*butane isomeride.

Apparently both these effects contribute to the differences observed, for H. R. Ing and W. H. Perkin [81] have now investigated the intermediate case, the condensation of $\alpha\alpha'$-dibromoglutaric ester, in which the carbethoxyl groups are present but the *gem*-dimethyl substituent is absent, and have observed the simultaneous occurrence of both *cyclo*propane and *cyclo*butane ring formation :



As would be expected from the great difference in the ease of formation of five- and four-membered rings, the corresponding condensation of $\alpha\alpha'$-dibromoadipic ester proceeds smoothly in one direction,[82] no *cyclo*butane derivative accompanying the *cyclo*pentane ester formed :



In the course of this work the interesting fact has been discovered that in the ring closures leading to the symmetrical esters (C) and (D), changes of configuration may take place. The dibromo-esters (A) and (B) each contain two equivalent asymmetric carbon atoms, and therefore exist in *meso*- and racemic modifications. During the condensations replacement occurs at each of these carbon atoms, which remain asymmetric and equivalent in the final product. Hence, if no change of configuration took place, the *meso*-bromo-ester should yield the *meso*-ring-ester, and the racemic bromo-ester the racemic ring-ester. The same products would be obtained if a

[81] *J.*, 1925, **127**, 2387.

[82] W. H. Perkin, jun., and E. Robinson, *J.*, 1921, **119**, 1393; A. W. Bernton, H. R. Ing, and W. H. Perkin, jun., *ibid.*, 1924, **125**, 1492.

change like the Walden inversion occurred at *both* asymmetric carbon atoms. If, however, configurative change occurred at one asymmetric carbon and not at the other, the *meso*-bromo-ester should yield the racemic ring-ester and *vice versa*. Such unsymmetrical inversions occur, because, in the first place, both the pure *meso*- and the pure racemic dibromoglutaric ester yield mixtures of the *meso*- and racemic ring-esters. Still more remarkable, however, is the fact that a complete inversion takes place in the very smooth condensation of *meso*-dibromoadipic ester to give the racemic *cyclo*pentane ester. Apparently the change of configuration does not precede the condensation in this case, because the *meso*-dibromo-ester is stable, and the tendency to isomeric change is in the other direction, namely, racemic⟶meso. The configurations of the ring esters were conclusively proved by the resolution of the racemic tribasic acids derived from them on hydrolysis;[83] those of the dibromoglutaric acids appear to follow from their synthesis[84] by the fission of cyclic compounds; and those of the dibromoadipic acids are established by the resolution of the racemic isomeride.[85]

In passing, it may be noted that the *cyclo*propane ester (E) readily changes by internal condensation into the dicyclic ketone (F), which can be isolated as its sodium compound (G). This is the simplest member of the five-carbon ring series of compounds in which intra-annular tautomerism has been shown to occur.

(F) $CH_2<\begin{matrix}C(CO_2R)\cdot CO\\ C(CO_2R)\cdot CH\cdot CO_2R\end{matrix}$ $\qquad$ $CH_2<\begin{matrix}C(CO_2R)\cdot C\cdot ONa\\ C(CO_2R)\cdot C\cdot CO_2R\end{matrix}$ (G)

Formation of cyclo*Propane Compounds by the Action of Alkalis on Bromo-acids.*—The method of producing *cyclo*propane compounds by reactions[86] such as

$$CR_2<\begin{matrix}CHBr\cdot CO_2Et\\ CH_2\cdot CO_2Et\end{matrix} \xrightarrow{(KOH)} CR_2<\begin{matrix}CH\cdot CO_2H\\ CH\cdot CO_2H\end{matrix}$$

$$CR_2<\begin{matrix}CHBr\cdot CO_2Et\\ CHBr\cdot CO_2Et\end{matrix} \xrightarrow[(EtOH)]{(KOH)} CR_2<\begin{matrix}C(OEt)\cdot CO_2H\\ CH\cdot CO_2H\end{matrix}$$

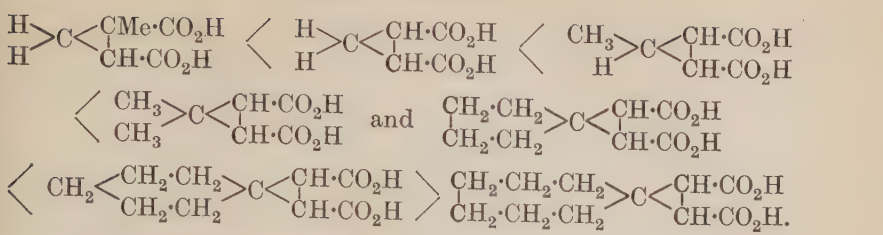
has recently been extended to several new cases. Ring closures of this character have been shown to be largely influenced by spatial differences due to substitution, and the order of facilitation of the reaction is as follows:

[83] W. H. Perkin, jun., and E. Robinson, *loc. cit.*; H. R. Ing and W. H. Perkin, jun., *loc. cit.*

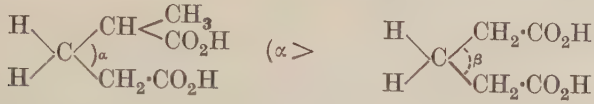
[84] J. Thiele, *Annalen*, 1901, **314**, 305; *A.*, 1901, i, 181.

[85] B. Holmberg and E. Müller, *Ber.*, 1925, **58**, 1601; *A.*, i, 1236.

[86] W. H. Perkin, jun., and J. F. Thorpe, *J.*, 1899, **75**, 48; 1901, **79**, 729.

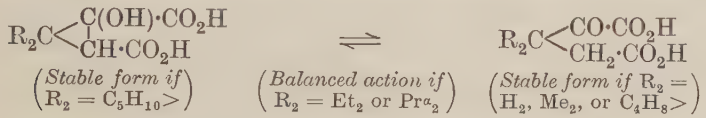


In the first of these cases [87] it is assumed, in conformity with other evidence,[88] that the branched chain residue in the glutaric acid has a greater space-filling capacity than the normal acetic acid residue, and thus tends to widen the angle at the central carbon atom :



If this be admitted, the whole series falls into line with the requirements of the spatial hypothesis, with the exception of the *cyclo*heptane compounds, the anomalous behaviour of which it seems impossible to account for except on the supposition that the *cyclo*heptane ring is puckered, or becomes so under the conditions in which the *cyclo*propane ring is formed.[89]

Further evidence of the abnormal influence of the *cyclo*heptane ring is derived from the fact that the *spiro*-compound is definitely less stable than its *cyclo*hexane analogue, as is shown from a study of the ring-chain tautomerism exhibited by its hydroxy-derivative. The relative stability of the individuals entering into the system



has been shown to be an important criterion of the effect of the substituents R_2 in modifying the stability of the *cyclo*propane ring, for whilst in the dihydrogen ($R_2 = H_2$), dimethyl ($R_2 = Me_2$), and *cyclo*pentane series ($R_2 = C_4H_8>$) the open-chain keto-acid is the stable modification, in the *cyclo*hexane series ($R_2 = C_5H_{10}>$) the strain in the three-membered ring is relieved to an extent which renders the hydroxy-ring compound the stable isomeride; inter-

[87] C. K. Ingold, *J.*, 1925, **127**, 387.

[88] C. K. Ingold and E. A. Perren, *ibid.*, 1921, **119**, 1582.

[89] J. W. Baker and C. K. Ingold, *ibid.*, 1923, **123**, 122; H. Meerwein, *J. pr. Chem.*, 1922, **104**, 161; *A.*, 1923, i, 221; H. Meerwein and J. Schäfer, *ibid.*, p. 289; *A.*, 1923, i, 324; F. Dickens, L. Horton, and J. F. Thorpe, *J.*, 1924, **125**, 1830.

mediate cases are known (*e.g.*, $R_2 = Et_2$) in which the two forms possess approximately equal stability. Now, if the *cyclo*heptane ring possesses a planar configuration, it should take its normal place in the series, and its *spirocyclo*propanol acid should be even more stable relatively to its keto-acid than is the case with the *cyclo*hexane compounds. It was found, however, that although the *cyclo*heptane *spiro*-hydroxy-acid was present in sufficient amount to be isolated (yield 1%), the keto-acid was the more stable individual.[90] These *cyclo*heptane compounds, therefore, closely resemble their *cyclo*pentane analogues, which contain an almost strain-free ring, and their behaviour accords with the view that the *cyclo*heptane ring exists in a multiplanar form.

A very remarkable series of anomalous reactions was encountered by W. Haerdi and J. F. Thorpe [91] when investigating the influence of a single phenyl substituent. The reaction of dibromo-β-phenyl-glutaric ester with alcoholic potash proceeded normally, giving a good yield of ethoxy-ring ester :

$$PhCH\langle \begin{matrix} CHBr\cdot CO_2R \\ CHBr\cdot CO_2R \end{matrix} \xrightarrow[EtOH]{KOH} PhCH\langle \begin{matrix} C(OEt)\cdot CO_2H \\ CH\cdot CO_2H \end{matrix}$$

but, in the case of the monobromo-compound, the corresponding ring-closure

$$PhCH\langle \begin{matrix} CHBr\cdot CO_2R \\ CH_2\cdot CO_2R \end{matrix} \longrightarrow PhCH\langle \begin{matrix} CH\cdot CO_2H \\ CH\cdot CO_2H \end{matrix}$$

could not be effected either with potash or with pyridine, owing to the fact that practically quantitative reduction to β-phenyl-glutaric acid (or ester) occurred in the presence of these reagents. This phenomenon has not been encountered before in analogous experiments with aliphatic halogenoglutaric esters, and must be attributed to the presence of the phenyl group. But the manner in which this group imparts to the bromine atom the type of activity observed, and why it does so only in the case of the monobromo-ester appear obscure notwithstanding recent discussions regarding such phenomena.

In view of the fact that a bromine atom in bromo*cyclo*propane acids is frequently rather difficult to remove, the quantitative reduction by potash of the bromo*cyclo*propane ester formulated below represents another remarkable instance of the influence of the phenyl group.[92]

[90] J. W. Baker, *J.*, 1925, **127**, 1678.
[91] *Ibid.*, p. 1237.
[92] W. Haerdi and J. F. Thorpe, *loc. cit.*

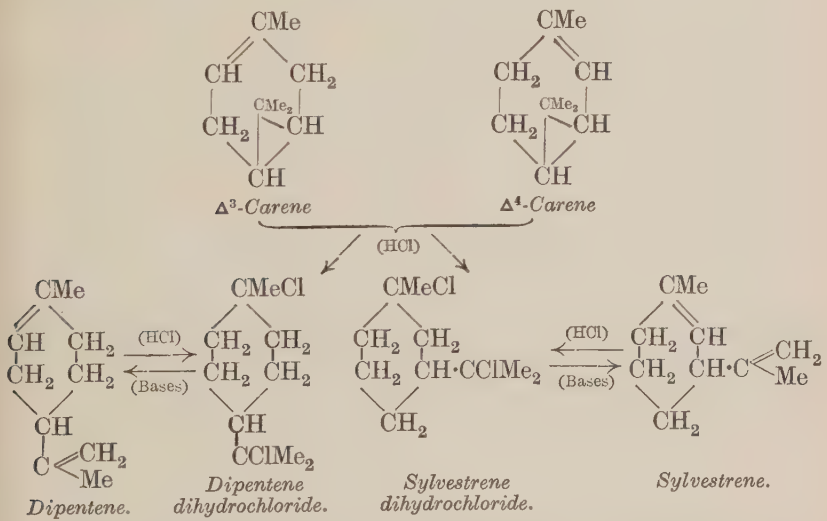
$$PhCH\langle \begin{matrix} CHBr\cdot CO_2Me \\ CH_2\cdot CO_2Me \end{matrix} \xrightarrow[(3KOH)]{} PhCH\langle \begin{matrix} CH_2\cdot CO_2K \\ CH_2\cdot CO_2K \end{matrix} + 2MeOH + KOBr$$

$$PhCH\langle \begin{matrix} CHBr\cdot CO_2Me \\ CH_2\cdot CO_2Me \end{matrix} \xrightarrow[(pyridine)]{} PhCH\langle \begin{matrix} CH_2\cdot CO_2Me \\ CH_2\cdot CO_2Me \end{matrix} + Br.$$

$$PhCH\langle \begin{matrix} CBr\cdot CO_2Me \\ CH\cdot CO_2Me \end{matrix} \xrightarrow[(3KOH)]{} PhCH\langle \begin{matrix} CH\cdot CO_2H \\ CH\cdot CO_2H \end{matrix} + 2MeOH + KOBr$$

The Occurrence of Carene and Sylvestrene.—So few derivatives of *cyclo*propane have been found in nature that the suggestion[93] that the carenes may prove to be widely distributed is of great interest.

Δ^3-Carene was first isolated by J. L. Simonsen from the essential oil of *Pinus longifolia* in 1920,[94] and shortly afterwards the same investigator obtained Δ^4-carene from the oil of *Andropogon Jwarancusa*.[95] On treatment with hydrogen chloride both these dicyclic terpenes yielded mixtures of dipentene dihydrochloride and sylvestrene dihydrochloride.[96]



Now the recorded occurrence of sylvestrene in nature has always seemed anomalous, since it is the only naturally occurring terpene derived from *m*-cymene, all other members of the series being *p*-cymene derivatives, and it was therefore thought probable[97] that

[93] B. S. Rao and J. L. Simonsen, *J.*, 1925, **127**, 2494.
[94] *Ibid.*, 1920, **117**, 571.
[95] *Ibid.*, 1922, **121**, 2294.
[96] *Ibid.* Compare *Indian Forest Rec.*, 1924, **10**, 161; *A.*, 1925, i, 1164.
[97] B. S. Rao and J. L. Simonsen, *loc. cit.*

although sylvestrene has been obtained from a considerable number of natural sources, it might not exist as such in nature, but might be formed during the process of purification.

Sylvestrene was first isolated from Swedish pine-tar oil, derived from *Pinus sylvestris*, by A. Atterberg,[98] who treated the appropriate fraction of the oil with hydrogen chloride, when sylvestrene dihydrochloride, m. p. 72°, was obtained. All subsequent investigators appear to have used this method of isolating sylvestrene from natural oils. It is significant that, in the course of his work, A. Atterberg [99] also isolated a hydrochloride of m. p. 50°, which is the m. p. of dipentene dihydrochloride, and that this substance was also encountered and recognised by J. Bertram and H. Wahlbaum [1] during the purification of sylvestrene through its dihydrochloride. Moreover, several workers noticed that the most characteristic reaction of sylvestrene, the deep blue colour formed when a drop of concentrated sulphuric acid is added to a solution of the hydrocarbon in acetic anhydride, was not given by those fractions of the original oil from which sylvestrene is obtained; on the other hand, those fractions gave a colour reaction now known to be characteristic of carene.[2]

An examination of the oil from Swedish *Pinus sylvestris* showed that this contained no sylvestrene, although a considerable quantity of Δ^3-carene was isolated through its sparingly soluble nitrosate. Similarly a sample of oil from *Pinus pumilio* contained Δ^3-carene but no sylvestrene.

From these results it would appear probable that sylvestrene does not occur as such in nature, and that carene, like its *cyclo*-butane isomeride, pinene, is widely distributed.

This proof of the absence of sylvestrene from natural products is of theoretical interest, since it removes the only exception to the view that the isoprene⟶geraniol union constitutes the first step in the formation of natural terpene structures.[3]

C. K. Ingold.

Part III.—Heterocyclic Division.

The work to be dealt with this year is greater in quantity and more varied in character than that of last year, two features which add to the difficulty of compiling this Report. A natural result of this

[98] *Ber.*, 1877, **10**, 1203; *A.*, 1877, i, 79. [99] *Loc. cit.*, p. 1208.

[1] *Arch. Pharm.*, 1893, **231**, 301; *A.*, 1893, i, 659.

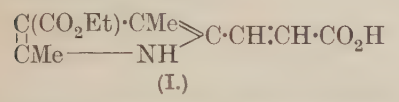
[2] *Idem, ibid.*; J. C. Umney, *Pharm. J.*, 1895, **55**, 167; *A.*, 1896, i, 380; Mörner, *Svensk Farm. Tids.*, 1909, 317, 1913.

[3] B. S. Rao and J. L. Simonsen, *loc. cit.* Compare *Ann. Report*, 1924, p. 102.

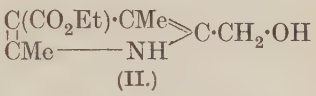
is that much work, especially in groups in which there are few workers, has had to be left unnoticed, at any rate for the present.

Pyrrole Derivatives.

In the previous Report mention was made of the application of the Gattermann reaction for the preparation of pyrrole aldehydes and the use of the latter for the synthesis of complex pyrroles.[1] Further examples of this are the preparation of 3-carbethoxy-2 : 4-dimethylpyrrole-5-vinyl-ω-carboxylic acid [2] (I) and a new series of tripyrrylmethanes.[3]



(I.)



(II.)

Reference may also be made now to a lengthy paper on the use of magnesylpyrrole in synthetic work, which will be of great assistance to workers in this field, not only for its wealth of experimental detail, but also for the full bibliography of previous work.[4]

The condensation of substituted pyrroles with formaldehyde in presence of alkali has been investigated and gives promise of useful development. Thus ethyl 2 : 4-dimethylpyrrole-3-carboxylate furnishes in this way the 5-hydroxymethyl derivative (II), which can be reduced to the aldehyde or, by the action of alkalis, acids, or boiling water, can be converted into the corresponding dipyrrylmethane.[5]

According to H. Fischer and H. Beller, the tetrapyrrylethanes obtainable from 2 : 3-dimethylpyrroles by the methods already referred to,[6] like those furnished by 2 : 4-dimethylpyrroles, are readily oxidised by ferric chloride to dipyrrylmethenes, in which respect both series differ from ætioporphyrin, whence it is concluded that in this pigment the four pyrrole nuclei are not simply linked together by the group C:C, but contain also two methine linkings.[7] Numerous papers have appeared on blood and bile pigments, but these are mainly of biological interest.

[1] *Ann. Reports*, 1924, **21**, 124.

[2] W. Küster, E. Brudi, and S. Koppenhöfer, *Ber.*, 1925, **58**, [*B*], 1014; *A.*, i, 972.

[3] H. Fischer and M. Heyse, *Annalen*, 1924, **439**, 246; *A.*, 1925, i, 76.

[4] B. Oddo, *Mem. R. Accad. Lincei*, 1923, [v], **14**, 510; *A.*, 1925, i, 296; see also *Gazzetta*, 1925, **55**, 235, 242; *A.*, i, 978, and T. N. Godnow and N. A. Naryschkin, *Ber.*, 1925, **58**, [*B*], 2703.

[5] H. Fischer and C. Nenitzescu, *Annalen*, 1925, **443**, 113; *A.*, i, 834; compare V. V. Tschelincev and B. V. Maksorov, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 748; *A.*, 1917, i, 164, and A. Einhorn, *Annalen*, 1905, **343**, 207; *A.*, 1906, i, 245.

[6] *Ann. Reports*, 1923, **20**, 138; 1924, **21**, 124.

[7] *Annalen*, 1925, **444**, 238; *A.*, i, 1333.

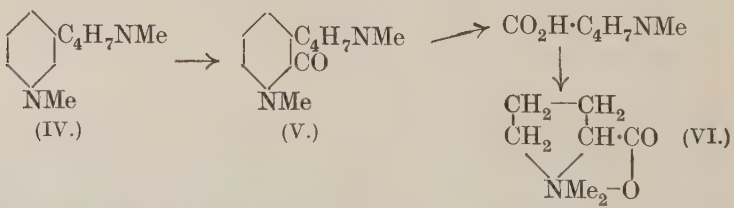
For reasons already fully discussed,[8] K. Hess and H. Fink assigned to the alkaloid cuskhygrine formula I. Later experiments by K. Hess and F. Anselm,[9] on the synthesis of one of its degradation products, di-*N*-methyldi-α-pyrrolidylmethane (II), led to a mixture of stereoisomerides, which furnished three methiodides, none of which was identical with either of those obtainable from the degradation product itself. An attempt has now been made [10] to obtain further information on this subject by the reduction of cuskhygrine. This creates a new asymmetric centre and results in the formation of two stereoisomeric secondary alcohols, both of which regenerate cuskhygrine on oxidation. A substance of formula I implies two *meso*-forms and one racemic form, whilst formula III, due to Liebermann and Cybulski,[11] requires one *meso*- and one racemic form. The formation of two dihydro-compounds indicates that cuskhygrine is either the racemic form of I or the *meso*-form of III.

(I.) $C_5H_{10}N{\cdot}CHAc{\cdot}C_5H_{10}N$ $\qquad$ $C_5H_{10}N{\cdot}CH_2{\cdot}C_5H_{10}N$ (II.)

$C_5H_{10}N{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}C_5H_{10}N$ (III.)

Exhaustive methylation of the two dihydrocuskhygrines leads to *n*-undecane and *n*-undecan-ζ-ol and thus lends support to formula III, since a substance of formula I should yield ε-ethylnonane and γ-*n*-butylheptan-β-ol.

Previous work on the oxidation of nicotine has usually led to the survival and isolation only of derivatives of the pyridine half of the molecule. P. Karrer and R. Widmer [12] find that on oxidation of *N*-methylnicotine (IV) with potassium ferricyanide *N*-methylnicotone (V) is formed, and this on oxidation with chromic acid yields *l*-hygric acid, $[\alpha]_D$ −80·12°, from which is obtainable by methylation *l*-stachydrine (VI) identical with the natural product from *Stachys tuberifera*, or that formed from *l*-proline by methylation.



It follows from this that *l*-proline, *l*-stachydrine, and *l*-nicotine all

[8] *Ann. Reports*, 1920, **17**, 126. [9] *Ibid.*, 1921, **18**, 118.
[10] K. Hess and R. Bappert, *Annalen*, 1925, **441**, 137, 151; *A.*, i, 424.
[11] *Ber.*, 1895, **28**, 578; *A.*, 1895, i, 310.
[12] *Helv. Chim. Acta*, 1925, **8**, 364; *A.*, i, 1084.

have the same lævo-configuration.[13] There still remains to be explained in this group the stereochemical relationship of betonicine to turicine, respectively *l*- and *d*-forms (probably not enantiomorphic) of 4-hydroxystachydrine.[14]

Pyridine Derivatives.

Most of the papers which come within this group relate to the preparation of comparatively simple derivatives of pyridine, some of which are of importance as primary materials for synthesis, or as possible degradation products from naturally occurring nitrogenous substances, but they do not call for comment here.

E. E. Blaise and M. Montagne [15] have found that whilst complex δ-diketones, containing electro-negative groups, undergo enolisation on treatment with ammonia and yield dihydropyridines, the simpler acyclic δ-diketones furnish *cyclo*hexenones under like conditions; thus γη-nonadione with ammonia yields exclusively 2-methyl-3-ethyl-Δ^2-*cyclo*hexen-1-one, but if ammonia is replaced by hydroxylamine hydrochloride, or, better, if the dioxime is heated with hydrochloric acid, 2 : 6-diethylpyridine is formed.

C. F. H. Allen [16] has found that the δ-ketonic nitrile (I) formed by the addition of phenyl styryl ketone to *p*-nitrophenylacetonitrile is converted by hydrogen bromide in acetic acid, but not by acetyl chloride, into 2-keto-4 : 6-diphenyl-3-*p*-nitrophenyltetrahydropyridine (III), which with nitrous acid gives 2-hydroxy-4 : 6-diphenyl-3-*p*-nitrophenylpyridine. Since water appears to be essential for the first part of this process, the change is presumed to take place by the addition of water thus :

$$\underset{\text{(I.)}}{NO_2\cdot C_6H_4\cdot CH(CHPh\cdot CH_2\cdot COPh)\cdot CN} \longrightarrow \underset{\text{(II.)}}{NO_2\cdot C_6H_4\cdot CH(CHPh\cdot CH_2\cdot COPh)\cdot CO\cdot NH_2} \longrightarrow \underset{\text{(III.)}}{NO_2\cdot C_6H_4\cdot CH(PhHC\cdot CH{=}CPh)\cdot CO\cdot NH}$$

and this view is supported by the fact that the cyanoacetamide additive product, $COPh\cdot CH_2\cdot CHPh\cdot CH(CN)\cdot CO\cdot NH_2$, is converted into the tetrahydropyridine derivative in presence of either acetyl chloride or dimethylaniline.[17]

B. D. Shaw [18] has confirmed his suggestion that pyridine on reduction by sodium and alcohol is first converted into 1 : 4-dihydro-

[13] Compare *Ann. Reports*, 1924, **21**, 61.

[14] J. A. Goodson and H. W. B. Clewer, *J.*, 1919, **115**, 929.

[15] *Compt. rend.*, 1925, **180**, 1760; *A.*, i, 835; compare E. Knoevenagel, *Annalen*, 1894, **281**, 25; *A.*, 1895, i, 48.

[16] *J. Amer. Chem. Soc.*, 1925, **47**, 1733; *A.*, i, 963; compare Kohler and Allen, *ibid.*, 1924, **46**, 1522; *A.*, 1924, i, 855.

[17] E. P. Kohler and B. L. Souther, *ibid.*, 1922, **44**, 2903; *A.*, 1923, i, 243.

[18] *J.*, 1925, **127**, 215; compare *Ann. Reports*, 1923, **20**, 147; 1924, **21**, 125.

pyridine, by the isolation of glutardialdehyde, as the dioxime, from the reduction liquor.

An interesting modification of Hofmann's reaction has been described.[19] When 1 : 2 : 6-triphenyl-4-piperidone, dissolved in benzene, is treated with bromine, it is converted into 1 : 3 : 5-tribromo-2 : 6-diphenyl-1-bromophenyl-4-piperidone (I), which when boiled in chloroform yields *p*-bromoaniline and dibenzylideneacetone dibromide (III). The following explanation of the reaction is given :

(I.) $C_6H_4Br\cdot NHBr<\begin{matrix}CHPh\cdot CHBr\\CHPh\cdot CHBr\end{matrix}>CO \longrightarrow$

$C_6H_4Br\cdot NH\cdot CHPh\cdot CHBr\cdot CO\cdot CHBr\cdot CHPhBr \xrightarrow{\text{with loss of } Br_2}$

$C_6H_4Br\cdot NH\cdot CHPh\cdot CHBr\cdot CO\cdot CH{:}CHPh.$

(II.) $C_6H_4Br\cdot NH_2Br\cdot CHPh\cdot CHBr\cdot CO\cdot CH{:}CHPh \xrightarrow{\text{with addition of HBr}}$

(III.) $C_6H_4Br\cdot NH_2,HBr + CHPhBr\cdot CHBr\cdot CO\cdot CH{:}CHPh$

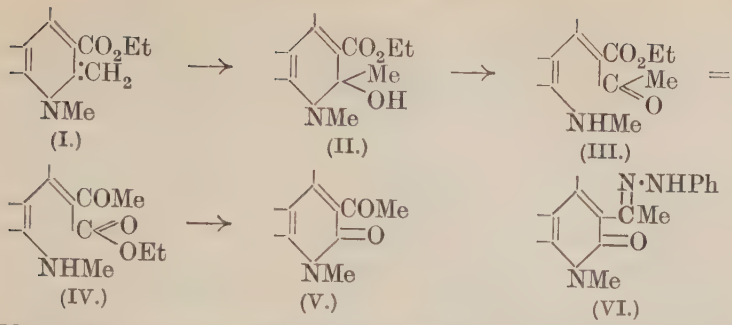
It is assumed that the hydrogen bromide necessary is formed by decomposition of part of the tribromo-compound (II), and that Hofmann's reaction always proceeds in this manner by formation of an unsaturated isomeride and ultimate transfer of the negative groups, resulting in decomposition.

Further progress has been made in the chemistry of methylenedihydropyridines. 2-*p*-Nitrobenzylpyridine methochloride is convertible by the general method into 2-*p*-nitrobenzylidene-1-methyldihydropyridine. This and its 4-*para*-isomeride are so unusually stable that a betaine-like structure involving the nitro-group is suggested, but this idea is scarcely tenable in view of the similar characteristics of the non-nitrated compounds. Benzylidene-2-benzylpyridine, $C_5H_4N\cdot CPh{:}CHPh$, obtained by condensing benzaldehyde with 2-benzylpyridine in presence of zinc chloride, furnishes a methiodide, which, on treatment with alkali, loses benzaldehyde and forms benzylidenemethyldihydropyridine. Stilbazole methiodide is similarly converted into benzaldehyde and 1-methyl-2-methylenedihydropyridine.[20] The reactions of the methylenedihydropyridines (I) derived from a series of ethyl 4-alkylpyridine-3 : 5-dicarboxylates have been investigated by O. Mumm and collaborators.[21] On suspension in water, they undergo a transformation represented by the following scheme :

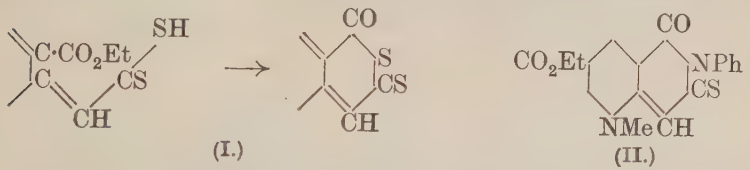
[19] P. Petrenko-Kritschenko and V. B. de Katzman, *J. Soc. Phys. Chim. Russe Univ. Leningrad*, 1924, **55**, 397; *A.*, 1925, i, 1094.

[20] E. Koenigs, K. Köhler, and K. Blindow, *Ber.*, 1925, **58**, [*B*], 933; *A.*, i, 833.

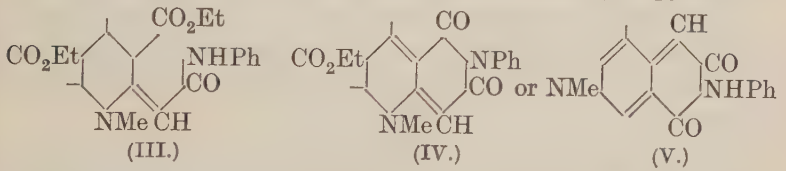
[21] *Annalen*, 1925, **443**, 272; *A.*, i, 964; compare *Ann. Reports*, 1924, **21**, 127.



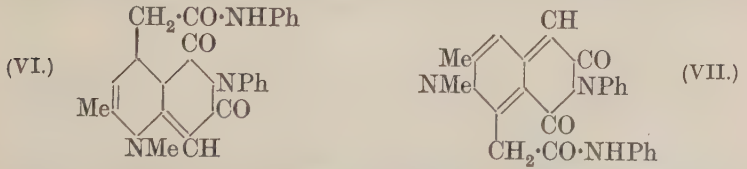
The product at stage (V) has been isolated. With phenylhydrazine in dry ether, a similar change takes place and the phenylhydrazone (VI) has been obtained. Reduction of the methides in alcohol, ethyl acetate, or hexane in presence of platinum sponge converts them into the corresponding 2-methyl-2 : 3-dihydropyridines. The authors represent as follows, the additive compounds [22] formed by the methides with carbon disulphide (I) and phenylthiocarbimide (II). The reaction with phenylcarbimide proceeds similarly, but



the initial products (III) can be isolated in this case and these on boiling with alcohol may furnish dicyclic derivatives (IV) or a mixture of (IV) and (V). 1 : 4 : 6-Trimethylmethylenedihydropyridine is



exceptional in combining with 2 mols. of phenylcarbimide, and the initial additive product yields two dicyclic isomerides (VI, VII).

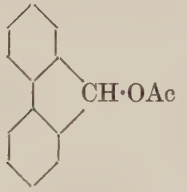
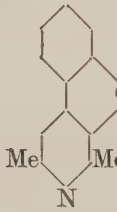


The commercial possibilities of nicotine as an insecticide are no doubt in part responsible for the activity in the synthesis of pyridyl-

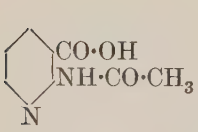
[22] Compare *Ann. Reports*, 1924, **21**, 127.

pyrroles. The initial materials are mucic acid, a convenient source of pyrrole which has become available commercially, and α- and γ-substituted pyridines, now readily made by the sodamide reaction. The methods used are essentially those of Pictet and his colleagues for the synthesis of nicotyrine and nicotine. All the authors [23] concerned seem to be agreed that when 2-aminopyridine is distilled with mucic acid the chief product is *N*-(2′-pyridyl)pyrrole, but the results recorded as obtained when this substance is subjected to pyrogenic isomerisation are discrepant, although if the reaction proceeds as in Pictet and Crepieux's case there appear to be only two possibilities.

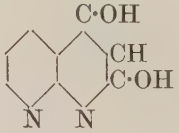
There was considerable activity during the year in the preparation of condensed pyridines. W. H. Mills, W. H. Palmer, and Miss M. G. Tomkinson, in the hope of elucidating the nature of the isomerism of the 9-acetoxy- and 9-amino-fluorenes (I) obtained by J. Schmidt and co-workers,[24] prepared pyridofluorene and certain of its unsymmetrically substituted derivatives (II). Attempts to resolve the latter were unsuccessful and thus failed to produce evidence for the non-coplanar configuration of the fluorene molecule, assumed to be necessary to explain the existence of Schmidt's isomerides.[25]

(I.)  (II.) 

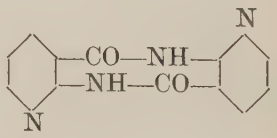
O. Seide [26] was unable to convert methyl 2-acetamidopyridine-3-carboxylate (I) into 2 : 4-dihydroxy-1 : 8-naphthyridine (II) by the action of sodium ethoxide, the only product being the anhydride of 2-aminopyridine-3-carboxylic acid (III).



(I.)



(II.)



(III.)

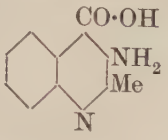
[23] J. P. Wibaut and others, *Rec. trav. chim.*, 1923, **42**, 1033; 1924, **43**, 526; *A.*, 1923, i, 1232; 1925, i, 75; A. E. Tschitschibabin and I. G. Bylinkin, *J. Russ. Phys. Chem. Soc.*, 1924, **55**, 100; *A.*, 1925, i, 1174; Chem. Fabrik auf Aktien (vorm. E. Schering), D.R.-P. 412168; *A.*, 1925, i, 1329.

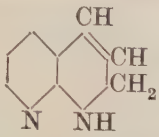
[24] *Ber.*, 1906, **39**, 3895; 1908, **41**, 1243; *A.*, 1907, i, 43; 1908, i, 415.

[25] *J.*, 1924, **125**, 2365; compare R. Kuhn and P. Jacob, *Ber.*, 1925, **58**, [*B*], 1432, 2232; *A.*, i, 1260, 1404.

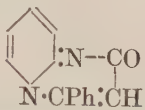
[26] *Ber.*, 1924, **57**, [*B*], 1806; *A.*, 1925, i, 72; compare L. Schmid and B. Bangler, *ibid.*, 1925, **58**, [*B*], 1971; *A.*, i, 1459.

Similarly, J. M. Gulland and R. Robinson [27] were unable to obtain naphthyridine derivatives from 3-amino-2-methylcinchoninic acid (IV) by the application of the Camps synthesis.

(IV.) 

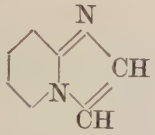


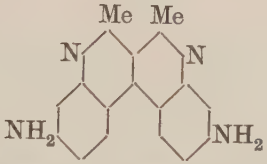
(V.)



(VI.)

Räth,[28] however, obtained 1 : 8-dihydronaphthyridine (V) by the action of bromoacetal on 2-amino-3-methylpyridine, but there is some doubt as to the constitution of his initial material, which differs in character from the 2-amino-3-methylpyridine prepared by O. Seide,[28] whose data are confirmed by A. E. Tschitschibabin.[28] From 2-aminopyridine, by the action of bromoacetaldehyde or its acetals, the latter author obtained pyriminazole (VII) (compare p. 155).

(VII.) 



(VIII.)

Palazzo and Tamburini's 4-phenyl-1 : 8-naphthyrid-2-one,[29] obtained by the action of sulphuric acid on 2-benzoylacetamidopyridine (or 1-benzoylacetamido-2-pyrimidine), is now shown [30] to be 4-keto-6-phenyl-1 : 2-divinylenedihydropyrimidine (VI), ring closure having occurred at the pyridine *N*-atom and not at the 3-carbon atom.

The copyrine synthesis referred to last year [31] has been extended by Gulland and Robinson [27] to the preparation of 10 : 15-diamino-1 : 8-dimethyldibenzocopyrine (VIII).

Quinoline Derivatives.

Useful modifications of the Doebner–von Miller quinaldine synthesis have been devised independently by C. Räth [32] and by F. A.

[27] *J.*, 1925, **127**, 1493; R. Camps, *Arch. Pharm.*, 1899, **237**, 659; *A.*, 1900, i, 31.

[28] *Ber.*, 1925, **58**, [*B*], 346; *A.*, i, 437; O. Seide, *ibid.*, 1924, **57**, [*B*], 1802; 1925, **58**, [*B*], 1733; *A.*, i, 72, 1328; A. E. Tschitschibabin, *ibid.*, pp. 1704, 1707; *A.*, i, 1328.

[29] *Atti R. Accad. Lincei*, 1911, [v], **20**, i, 37; *A.*, 1911, i, 327.

[30] O. Seide, *Ber.*, 1925, **58**, [*B*], 352; *A.*, i, 437; compare *Ann. Reports*, 1924, **21**, 126, and H. Finger and F. Kraft, *Ber.*, 1924, **57**, [*B*], 1950; *A.*, 1925, i, 73.

[31] *Ann. Reports*, 1924, **21**, 140 (ref. 68).

[32] *Ber.*, 1924, **57**, [*B*], 550, 715; *A.*, 1924, i, 555, 667; compare Heller, *ibid.*, p. 764; *A.*, 1924, i, 768.

Mason.[33] Both authors prepared 1 : 2-dihydroquinaldine by reactions which may be shortly represented by the following linear scheme :

$$CH_3\cdot CHBr\cdot CH(OEt)_2 + CH_3\cdot C_6H_4\cdot NH_2(1:2) \longrightarrow C_6H_4\langle \begin{matrix} CH{=}CH \\ NH{-}CHMe \end{matrix}$$

(I.)

$$CHMeCl\cdot CH_2\cdot CH(OEt)_2 + Ph\cdot NH_2 \longrightarrow NHPh\cdot CHMe\cdot CH_2\cdot CH(OEt)_2$$

(II.)

In Räth's case (I), ring closure is effected by heating at 260° in a sealed tube and in Mason's (II) by treatment with phosphoric oxide in benzene solution; in the latter reaction, hydrochloric acid, acetic acid, or acetic anhydride is ineffective, as is also heating under pressure as adopted in (I). Räth has investigated the reaction in a number of other instances with the following results :

Amine.	*Halogenated product.*	*Substance formed.*
o-Toluidine.	Bromoacetal.	1 : 2-Dihydroquinoline.
Methyl-*o*-toluidine.	β-Bromopropionacetal.	1-Methyl-1 : 2-dihydroquinoline.
1 : 2-Dihydroquinoline.	Ethylene chlorohydrin.	1-(β-hydroxyethyl)-1 : 2-dihydroquinoline.
o-Aminopropylbenzene.	Chloroacetal.	4-Ethyl-1 : 2-dihydroquinoline and 3-ethoxy-4-ethyl-1 : 2 : 3 : 4-tetrahydroquinoline.
Aniline.	β-Chloropropionacetal.	4-Ethoxytetrahydroquinoline with some dihydroquinoline.
Ethylaniline.	Bromoacetal.	1-Ethylindole with some 3-ethoxy-1-ethyl-2 : 3-dihydroindole.

Aniline does not condense with styryl methyl ketone under Doebner–von Miller conditions, and the best yield (12·8%) of 2-phenyl-4-methylquinoline results when the two reagents are heated with a minute quantity of hydrochloric acid in a closed vessel at 135° for 5 hours. A number of substituted 2-phenylquinolines were thus prepared, but no quinoline derivatives could be obtained from sulphanilic acid, *o*- and *p*-aminobenzaldehydes, phenylenediamine, amino-*p*-cresol, aminosalicylic acid, α-naphthylamine, tetrahydro-β-naphthylamine, β-aminoanthracene, or β-aminoanthraquinone, and only traces from *o*- and *p*-nitroanilines.[34]

The direct and the indirect conversion of the toluene-*p*-sulphonyl derivative of β-anilinopropionic acid into 4-keto-1 : 2 : 3 : 4-tetrahydroquinoline (4-dihydroquinolone) by the action of (*a*) phosphoric

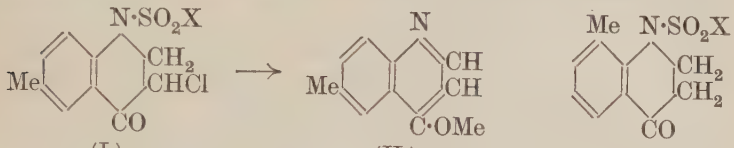
[33] *J.*, 1925, **127**, 1032.

[34] H. John and others, *J. pr Chem.*, 1925, [ii], **111**, 65, 83; *A.*, i, 1451, 1452.

oxide and (*b*) phosphoryl chloride followed in each case by hydrolysis, referred to last year,[35] have been further investigated [36] by extension to the corresponding substances,

$$C_6H_4Me{\cdot}N(SO_2{\cdot}C_7H_7){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H,$$

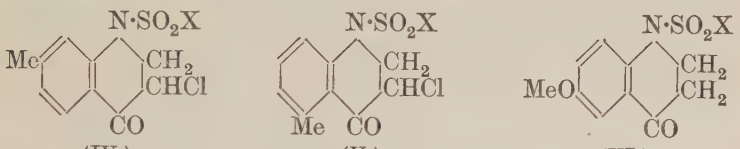
derived from *o*-, *m*-, and *p*-toluidines. The *p*-toluidine compound behaves like its lower homologue, giving with phosphoryl chloride the 3-chloro-compound (I. $SO_2X = SO_2{\cdot}C_7H_7$) which, on acid hydrolysis, yields the corresponding 4-keto-6-methyl-1 : 2 : 3 : 4-tetrahydroquinoline and on boiling with methyl-alcoholic potassium hydroxide is converted into 4-methoxy-6-methylquinoline (II).



(I.) (II.) (III.)

In the case of the *o*-toluidine derivative none of the 3-chloro-compound is formed and only a little of the 4-keto-8-methyl-1 : 2 : 3 : 4-tetrahydroquinoline and its toluene-*p*-sulphonyl derivative (III). The latter is anomalous in behaviour and on boiling with acids suffers ring scission, producing *o*-toluidine and β-*o*-toluidinopropionic acid.

With the *m*-isomeride, the results are like those with the lower homologue, but two 3-chloro-derivatives (IV) and (V) are formed,



(IV.) (V.) (VI.)

both of which undergo hydrolysis and lose chlorine on boiling with hydrochloric acid, yielding the 4-keto-5- and -7-methyltetrahydroquinolines, respectively.

When, in place of the toluidines, *p*-anisidine and *p*-phenetidine were used, the action proceeded as in the case of aniline and *p*-toluidine, but the amount of 3-chloro-derivatives formed in these cases was small; thus *p*-anisidine gave 10% of the chloro-product, the rest being the toluene-*p*-sulphonyl-6-methoxyketotetrahydroquinoline (VI).

An attempt to extend this reaction to the preparation of 4-keto-tetrahydro*iso*quinoline derivatives from toluene-*p*-sulphonylbenzylaminoacetic acid, $CH_2Ph{\cdot}N(SO_2X){\cdot}CH_2{\cdot}CO_2H$, was unsuccessful.

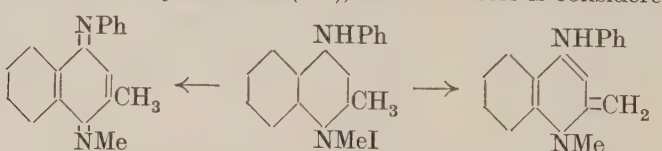
[35] *Ann. Reports*, 1924, **21**, 129.

[36] G. R. Clemo and W. H. Perkin, jun., *J.*, 1925, **127**, 2297.

On treatment with sodamide in presence of xylene, quinoline yields 2-aminoquinoline in about 40% yield, but the reaction proceeds less smoothly than with pyridine. On nitration, 2-aminoquinoline furnishes a stable 2-nitroaminoquinoline, which is converted by sulphuric acid at 130° into 6-nitro-2-aminoquinoline, and from 4-aminoquinoline a 6-nitro-derivative is similarly obtainable.[37] No evidence was obtained of the nitro-group remaining in the pyridine ring as it does when nitroaminopyridines are isomerised in like manner.

Arising out of Späth's synthesis of the angostura alkaloids,[38] J. Tröger and co-workers find that when 2- and 3-methoxyquinaldines condense with aromatic aldehydes, the products do not form crystalline salts, but this is not the case when the methoxyl group is in the 4-position or in the benzene nucleus.[39] With 2-methoxylepidine, demethylation occurs and condensation products of the hydroxy-base are formed, which also yield amorphous salts. Unmethylated hydroxyquinaldines and hydroxyaldehydes impede or prevent condensation; thus in Späth and Brunner's synthesis of cusparine [40] no condensation takes place if 4-hydroxy-2-methylquinoline is substituted for 4-methoxy-2-methylquinoline or if salicylaldehyde is employed in place of piperonal

Hydrogen halide can conceivably be eliminated from 4-aminoquinaldinium salts (I) in two ways, *viz.*, with the formation of an imino-base (II) or a methylene base (III), and the latter is considered the



(II.) (I.) (III.)

more probable; thus 4-anilinoquinaldine methiodide (I), on warming with aqueous sodium hydroxide, yields a yellow base, which is regarded as 4-anilino-1-methyl-2-methylene-1 : 2-dihydroquinoline.[41]

The same authors show that 4-chloroquinaldine methiodide with sodium carbonate or ammonia, in presence of alcohol, yields a violet solution, which slowly deposits steel-blue crystals of a dye, $C_{22}H_{20}N_2ClI$. This has the properties of an *iso*cyanine and is believed to be formed in the following way :

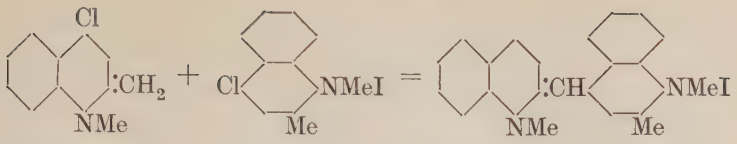
[37] A. E. Tschitschibabin and others, *Ber.*, 1925, **58**, [*B*], 803; *A.*, i, 838.

[38] *Ann. Reports*, 1924, **21**, 131.

[39] *J. pr. Chem.*, 1925, [iii], **109**, 88; **110**, 86; *A.*, i, 432, 974; compare E. Späth and H. Eberstaller, *Ber.*, 1924, **57**, [*B*], 1687; *A.*, 1924, i, 1335.

[40] *Ber.*, 1924, **57**, [*B*], 1243; *A.*, 1924, i, 1226.

[41] O. Fischer, E. Diepolder, and E. Wölfel, *J. pr. Chem.*, 1925, [ii], **109**, 59; *A.*, i, 438.

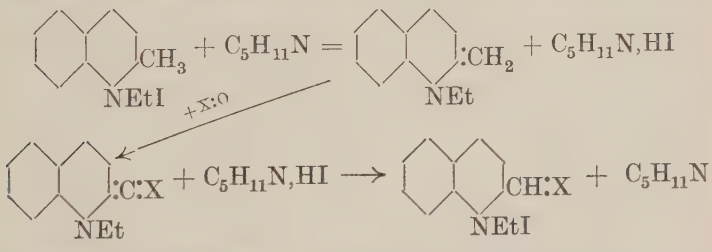


The same dye was probably obtained by Friedel by the action of phosphoryl chloride on acetomethylanilide. In this case, it is suggested that the dichloro-derivative, $NMePh{\cdot}CCl_2Me$, first formed condenses with itself, giving the product

$$NMePh{\cdot}CMe{:}CH{\cdot}CCl_2{\cdot}NMePh,HCl,$$

from which, by ring closure with loss of methylaniline, 4-chloroquinaldine is formed. The products isolated from the dye mother-liquors confirm this view of the mechanism of the reaction.[42]

The idea that the enhanced reactivity characteristic of methyl groups adjacent to the nitrogen atom in heterocyclic bases might be due to the capacity of the system $-N{=}CMe-$ to pass into the system $-NH{\cdot}C(:CH_2)-$ was raised by W. H. Mills and J. L. B. Smith three years ago,[43] and has now been subjected to detailed experimental investigation by W. H. Mills and R. Raper.[44] The reactivity is greater in the quaternary salts than in the bases themselves, and the condensations which result from this enhanced reactivity are brought about in presence of strong bases such as piperidine. It is supposed, therefore, that in a solution containing quinaldine ethiodide, piperidine as a condensing agent, and a reactive substance of the type X:O such as benzaldehyde, stage I of the reaction consists in the removal of hydrogen iodide as piperidine hydriodide, with the formation of some methylene base, and stage II in the condensation of the methylene base with X:O to form an intermediate basic product which then removes hydrogen iodide from piperidine hydriodide, regenerating piperidine and forming the new quaternary salt :



[42] O. Fischer, A. Müller, and A. Vilsmeier, *J. pr. Chem.*, 1925, [ii], **109**, 69; *A.*, i, 439; compare C. Friedel, *Bull. Soc. chim.*, 1894, [3], **11**, 1027; *A.*, 1895, i, 423; also A. Kaufmann and E. Vonderwahl, *Ber.*, 1912, **45**, 1404; *A.*, 1912, i, 502.

[43] *Ann. Reports*, 1922, **19**, 156.

[44] *J.*, 1925, **127**, 2466; compare Vongerichten and Höfchen, *Ber.*, 1908, **41**, 3054; *A.*, 1908, i, 914, and König, *ibid.*, 1922, **55**, 3301; *A.*, 1922, i, 1188.

The possibility of this mechanism in the case of the condensation of quinaldinium salts with aldehydes and with nitroso-compounds has been demonstrated by the isolation in a typical case of each intermediate compound or of a derivative, which leaves little doubt as to the nature of the reaction.

A series of carbocyanines (I) has been reduced to the corresponding methylenediquinaldine (II) dialkyliodides, further demonstrating the relationship already suggested [45] as existing between them.

$$\underset{\text{(I.)}}{C_9H_6NR{:}CH{\cdot}CH{:}CH{\cdot}C_9H_6NR} \longrightarrow \underset{\text{(II.)}}{C_9H_6NR{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}C_9H_6NR}$$

The synthesis of compounds allied to the cinchona alkaloids has been continued, but the products are of biological rather than new chemical interest.[46] There has been a certain renewal of interest in the cinchona alkaloids themselves. Quinotoxine oxime has been prepared and reduced to aminoquinotoxine.[47] Attempts to introduce an amino-group into the vinyl side chain of quinine by direct methods were unsuccessful, but phthalylamido- and benzenesulphonamido-derivatives of quinine were made by treating quinine chloride with alkali derivatives of phthalimide and benzenesulphonamide, respectively. The acyl groups were removed with difficulty, but some aminoquinine sulphate was obtained and converted into a quaternary base, $C_{20}H_{23}ON_2{\cdot}NMe_2OH$, which was isolated as the picrate,[48] An interesting series of copper derivatives of quinine has also been described.[49]

When the phenolic hydroxyl group in cupreine is methylated, quinine is formed, but the latter on demethylation yields apoquinine in place of cupreine; hydroquinine on the contrary yields hydrocupreine. The difference between apoquinine and cupreine is therefore probably connected with the vinyl group in quinine, and in confirmation of that view it has now been shown that apoquinine, unlike cupreine, is not hydrogenated in presence of nickel and the relationship between the two is probably not stereochemical.[50]

β-*iso*Quinine is stated to be 3-ethylidene-8-quinuclidyl-(6′-methoxy-4′-quinolyl)methanol.[51] Like quinine, it is convertible, by methods

[45] (Miss) F. M. Hamer, *J.*, 1925, **127**, 211.

[46] L. Ruzicka, C. F. Seidel, and F. Liebl, *Helv. Chim. Acta*, 1924, **7**, 995; *A.*, 1925, i, 289.

[47] S. Fränkel and N. Diamant, *Ber.*, 1925, **58**, [*B*], 554; *A.*, i, 574.

[48] S. Fränkel, C. Tritt, M. Mehrer, and O. Herschmann, *ibid.*, p. 544; *A.*, i, 573.

[49] F. Erben, *ibid.*, p. 468; *A.*, i, 573.

[50] G. Giemsa and K. Bonath, *ibid.*, p. 87; *A.*, i, 291; compare S. Fränkel and C. Buhlea, *ibid.*, p. 559; *A.*, i, 573.

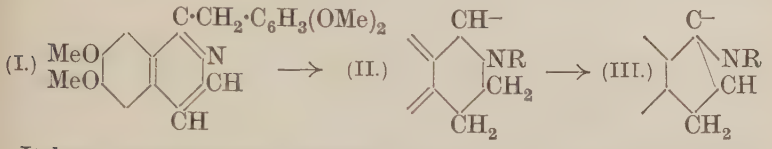
[51] J. Suszko, *Rocz. Chem.*, 1925, **5**, 358; *A.*, i, 1448; compare Lippmann and Fleissner, *Monatsh.*, 1891, **12**, 332; 1893, **14**, 554; *A.*, 1892, i, 82; 1893, i, 738; Böttcher, *ibid.*, 1911, **32**, 793; *A.*, 1911, i, 1011.

that are virtually standardised for this series of alkaloids,[52] into (1) a quinotoxine, which in this case is β-(3-ethylidene-4-piperidyl)ethyl 6′-methoxyquinolyl ketone and (2) a *N*-methylquinotoxine.

Niquine, $C_{19}H_{24}O_2N_2$, obtained as a by-product in the preparation of β-*iso*quinine, is a secondary-tertiary base, possesses one ethylenic linking, and probably a free hydroxyl group.[53]

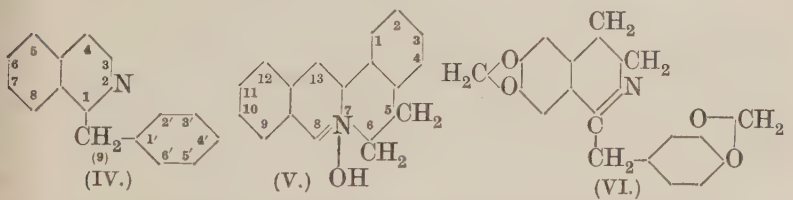
iso*Quinoline Derivatives.*

Work in this group has as usual been almost entirely confined to the *iso*quinoline alkaloids. When papaverine (I) or *N*-methylpapaverinium salts are reduced by tin and hydrochloric acid, there is produced, in addition to the tetrahydro-derivatives (II; R = H or Me) expected, a small amount of the 2 : 4-dihydro-derivatives (III), pavine and *N*-methylpavine :



It has now been shown [54] that *iso*quinoline, 1-benzyl*iso*quinoline or its methiodide, and 6 : 7-dimethoxy*iso*quinoline or its methiodide, are all reduced, in some instances almost quantitatively, to the tetrahydro-derivatives and no reduction product of the pavine type was obtained. The formation of the latter in the case of papaverine is therefore not due either to the presence of the two methoxyl groups in the *iso*quinoline nucleus, or to the attachment of the benzyl group in position 1.

The parent substances of the alkaloids berberine and papaverine are represented by formulæ (IV) and (V) and the names "protopapaverine" and "protoberberine" have been suggested for them, to simplify the nomenclature of a number of synthetic bases of this type, which have been prepared.[55]



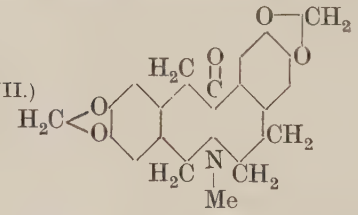
In 1913, H. Decker and his colleagues [56] described "1-piperonylnorhydrastinine," to which they assigned formula (VI), as being

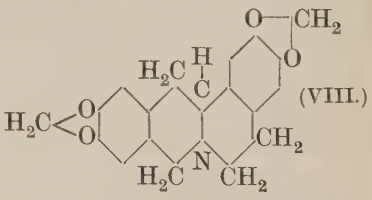
[52] See *Ann. Reports*, 1918, **15**, 113; 1920, **17**, 117.
[53] Compare *Ann. Reports*, 1924, **21**, 132.
[54] R. Forsyth, C. J. Kelly, and F. L. Pyman, *J.*, 1925, **127**, 1659.
[55] J. S. Buck, W. H. Perkin, jun., and T. S. Stevens, *ibid.*, p. 1462.
[56] *Annalen*, 1913, **395**, 299; *A.*, 1913, i, 289.

produced by the action of phosphoryl chloride in toluene on homopiperonoylhomopiperonylamine. Repetition of this experiment has resulted in the isolation of a different product, 6 : 7 : 3′ : 4′-bismethylenedioxy-3 : 4-dihydroprotopapaverine, to which formula (VI) is correctly assigned. This substance, like other 1-benzyldihydro*iso*quinolines, is readily oxidised on exposure to air to the 9-keto-derivative, which has the properties of Decker's substance.[55] By the insertion of a $-CH_2-$ linking between positions 2 and 2′ or 2 and 6′ in protopapaverine (IV), protoberberine (V) can be produced. It is probably carbon atom 6′ which reacts in preference to 2′, and when the benzyl group is substituted in the nucleus this results in the production of the pseudo-series of alkaloids, ψ-berberine, ψ-protopine (VII), etc.,[57] and it is probably this series to which the following substances belong.

The 6 : 7 : 3′ : 4′-bismethylenedioxy-3 : 4-dihydroprotopapaverine (VI) referred to above, on reduction yields the corresponding tetrahydro-compound, which on condensation with formaldehyde furnishes 2 : 3 : 10 : 11-bismethylenedioxytetrahydroprotoberberine (VIII). The latter is oxidised in the normal way by iodine to the corresponding protoberberinium iodide, from which, *via* the chloride, by the action of potassium hydroxide solution, the corresponding oxyprotoberberine and dihydroprotoberberine are obtainable [55] in the same manner as with berberinium chloride, where the analogous products are oxyberberine and dihydroberberine.

(VII.)

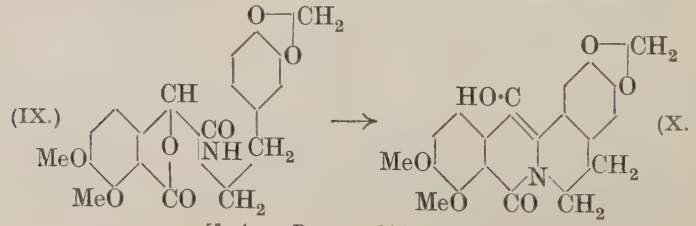




(VIII.)

The work on berberine referred to last year [57] has made it necessary to find a new synthetical proof of the constitution of berberine. This has been achieved by using the β-piperonylamide of meconincarboxylic acid (IX), which on prolonged treatment with phosphoryl chloride gave, in a preliminary experiment, dioxyberberine (X) and,

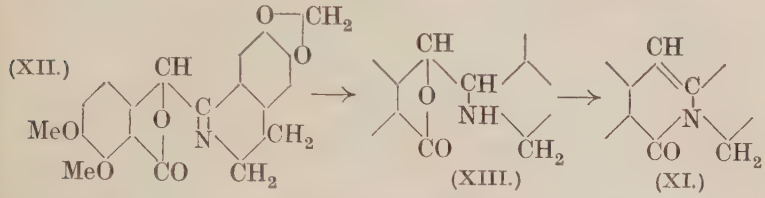
(IX.)



(X.)

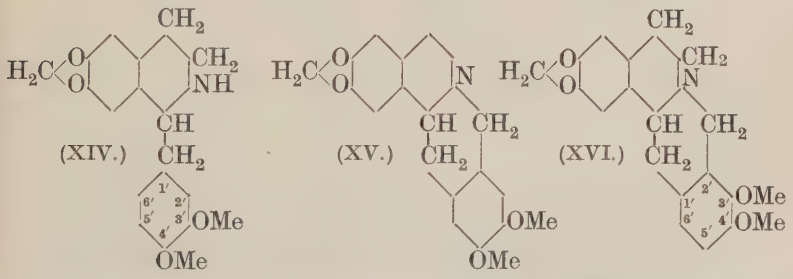
[57] *Ann. Reports*, 1924, **21**, 134.

in further trials with larger quantities, oxyberberine (XI) *via* a product, provisionally represented by formula (XII), which on reduction with zinc dust in boiling acetic acid, furnished oxyberberine (XI), probably through (XIII) as an intermediary.



Although a full explanation of the reactions involved cannot yet be given, this synthesis establishes the accuracy of the formula assigned to oxyberberine on many points and in particular leaves no doubt as to the position of the methoxyl groups. Oxyberberine on electrolytic reduction yields tetrahydroberberine, from which berberine can be prepared, and consequently the synthesis confirms the formulæ assigned to berberine and the alkaloids canadine, palmatine, etc., derivable from it.[58]

Among other attempts to synthesise berberine reference may be made to one having veratrylnorhydrohydrastinine (XIV) as a starting point.[59] It has been shown already that when this substance is treated with formaldehyde and hydrochloric acid, interaction occurs with the 6′- instead of the 2′- carbon atom and tetrahydro-ψ-berberine (XV) results. When the 6′-carbon atom is blocked by a substituent, a nitro-group or a bromine atom, to force interaction with the 2′-carbon atom, condensation occurs but in neither case was the expected tetrahydroberberine derivative (XVI) formed.

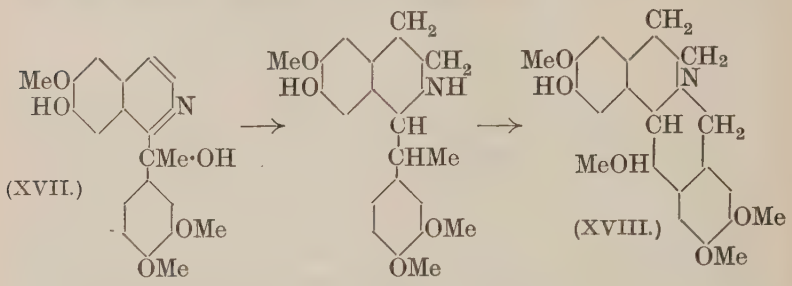


In the course of this work, it was noted that tetrahydroberberine readily nitrates in position 6′ (XVI), whilst tetrahydro-ψ-berberine (XV) does not nitrate but is oxidised by nitric acid. In similar

[58] W. H. Perkin, jun., J. N. Rây, and R. Robinson, *J.*, 1925, **127**, 740; compare E. Späth and H. Quietensky, *Ber.*, 1925, **58**, [*B*], 2267; *A.*, 1926, **A**, 82.

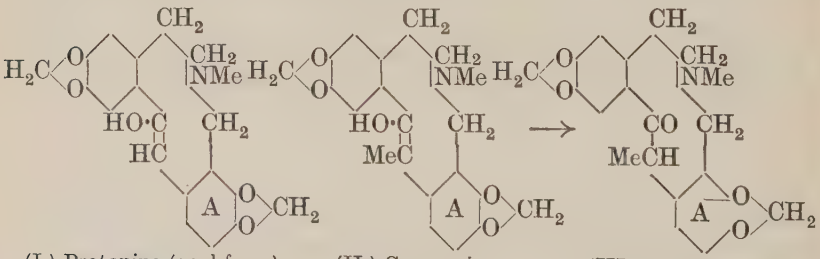
[59] R. D. Haworth and W. H. Perkin, jun., *J.*, 1925, **127**, 1448.

attempts to use 7-demethylomethylpapaverinol (XVII) as a starting point for the synthesis of corydaline, only a ψ-corydaline derivative, 7-demethylo-ψ-corydaline (XVIII), resulted.[60]



Corydaline is the principal alkaloid found in the tubers of *Corydalis tuberosa*, in which it occurs associated with a dozen or more other alkaloids, on which much work has been expended and to all of which constitutional formulæ have now been assigned. The least known members of this series, corycavidine, $C_{22}H_{25}O_5N$, corycavamine, $C_{21}H_{21}O_5N$, and corycavine, $C_{21}H_{21}O_5N$, form a subgroup of closely related bases.

A protopine (I) type of formula has been suggested [61] for corycavine (II) and it is now shown [62] that the other two bases are of similar constitution; corycavamine is represented as the keto-form of corycavine, since it is converted into that substance by heating at



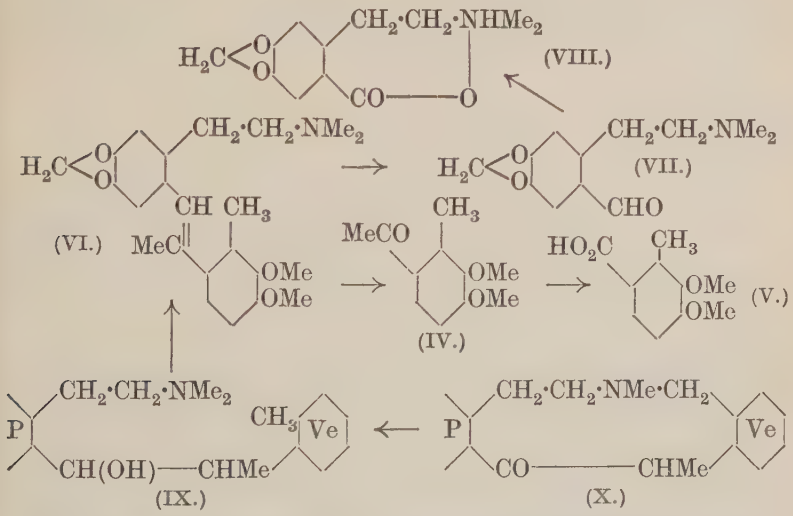
(I.) Protopine (enol form). (II.) Corycavine (enol-form). (III.) Corycavamine (keto-form).

its melting point, and both alkaloids on treatment with methyl iodide yield the same methine base, whilst corycavidine differs from corycavine in having the dioxymethylene group in ring A (formula II) replaced by two methoxyl groups.

The preliminary observations [63] made on corycavidine are all in

[60] R. D. Haworth and W. H. Perkin, jun., *J.*, 1925, **127**, 1453.
[61] J. Gadamer and F. v. Bruchhausen, *Arch. Pharm.*, 1922, **260**, 113.
[62] F. v. Bruchhausen, *ibid.*, 1925, **263**, 570.
[63] J. Gadamer, *ibid.*, 1911, **249**, 30; *A.*, 1911, i, 318.

harmony with this view of its constitution, and, like other alkaloids of similar constitution, the natural *d*-form (m. p. 212°) changes into an inactive form (m. p. 193°) on the application of heat. The new data brought forward may be summarised thus. Acetic anhydride converted the base mainly into the inactive form, but also produced some *N*-acetyl derivative and a small amount of a yellowish-red quaternary base, and phosphoryl chloride, which converts corycavine quantitatively into the corresponding quaternary base, only acted on corycavidine at temperatures high enough to produce action in the dioxymethylene group. Reduction of the methylated product gave an optically active tetrahydromethylcorycavidine, which was converted into an inactive anhydro-base by acetyl chloride; this is assumed to be due to the presence of the group $\cdot CH_2 \cdot CH(OH)\cdot$. Oxidation of this anhydro-base furnished methylacetoveratrone (IV); methylveratric acid (V); a nitrogen-free substance, m. p. 243°, for which a formula derived from (VI) by the replacement of the chain $\cdot CH_2 \cdot CH_2 \cdot NMe_2$ by a carboxyl group is proposed; *N*-methylhydrastinine (VII), also obtained in the oxidation of anhydroprotopine;[61] and the acid (VIII) corresponding to (VII).



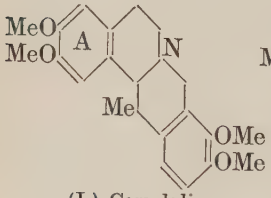
From these, the structure (VI) representing anhydromethylcorycavidine is built up and from this that of tetrahydromethylcorycavidine, represented by the condensed formula (IX), in which P and Ve represent the piperonyl and veratryl rings, respectively, and so back to corycavidine (X). The validity of the formula is supported by a number of confirmatory data.

Two other minor corydalis alkaloids, corybulbine and *iso*cory-

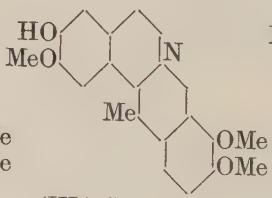
bulbine, $C_{21}H_{25}O_4N$, are both convertible into corydaline, $C_{22}H_{27}O_4N$, by nascent diazomethane, and all three alkaloids yield the same *apo*corydaline when boiled with hydriodic acid, so that the two minor alkaloids can only differ from each other in the position of a phenolic hydroxyl group, and from corydaline in the replacement of a methoxyl by a hydroxyl group. Both corybulbine and *iso*-corybulbine yield ethyl ethers, which on drastic oxidation furnish the methyl ethyl ether of nor-*m*-hemipinic acid, so that in both cases the –OH group must be in ring A (I, II, III). This acid has been synthesised from (*a*) 3-methoxy-4-ethoxybenzaldehyde and (*b*) 4-methoxy-3-ethoxybenzaldehyde by methods involving ring closure to the corresponding dihydro*iso*quinoline and oxidation of this to the required acid, which is identical in both cases. Further, on gentle oxidation the two ethyl ethers yield homologues of corydaldine :

corybulbine ⟶ 7-methoxy-6-ethoxy-1-keto-1 : 2 : 3 : 4-tetrahydro*iso*quinoline
*iso*corybulbine ⟶ 6-methoxy-7-ethoxy-1-keto-1 : 2 : 3 : 4-tetrahydro*iso*quinoline
corydaline ⟶ 6 : 7-dimethoxy-1-keto-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (corydaldine)

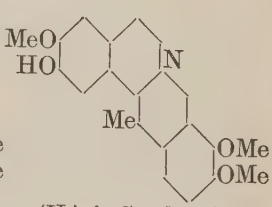
Both have been synthesised and shown to yield the same methyl ethyl ether of nor-*m*-hemipinic acid on further oxidation. The relationship of the three alkaloids must therefore be as follows : [64]



(I.) Corydaline.



(III.) Corybulbine.

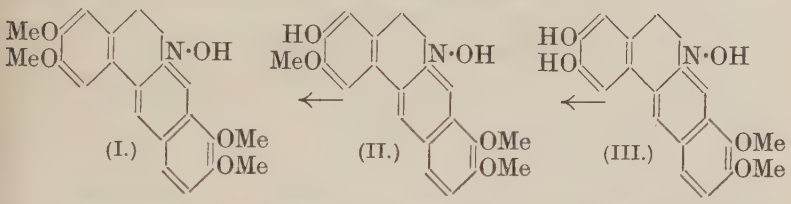


(II.) *iso*Corybulbine.

This method has also been used to determine the position of the free hydroxyl group in corypalmine, $C_{20}H_{23}O_4N$, another of the minor alkaloids of corydalis, which is known to yield *d*-tetrahydropalmatine, $C_{21}H_{25}O_4N$, on methylation.[65] The ethyl ether of corypalmine on oxidation with cold alkaline permanganate yields 7-methoxy - 6 - ethoxy - 1 - keto - 1 : 2 : 3 : 4 - tetrahydro*iso*quinoline, whence it is clear that the hydroxyl group must be in position 6 in the upper *iso*quinoline nucleus as in formula II (below) for jatrorrhizine and that corypalmine is in fact *d*-tetrahydrojatrorrhizine.

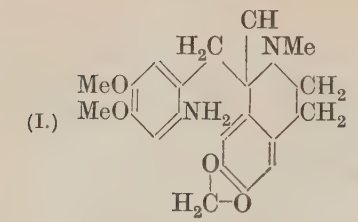
[64] E. Späth and A. Dobrowsky, *Ber.*, 1925, **58**, [*B*], 1274; *A.*, i, 1085; compare F. v. Bruchhausen and K. Saway, *Arch. Pharm.*, 1925, **263**, 602.
[65] E. Späth and E. Mosettig, *Ber.*, 1925, **58**, [*B*], 2133; *A.*, i, 1447.

By the same method, described above, it has been shown [66] that palmatine (I) is the methyl ether of jatrorrhizine (II), with which it occurs in Calumba root, and that the free hydroxyl group in the latter base occupies position 6 in the upper *iso*quinoline nucleus (II). Feist's columbamine from the same source is shown to be mainly palmatine, but the isolation of a third alkaloid is foreshadowed for which this name is reserved. The constitution of palmatine has already been established by its synthesis from berberine,[67] from which it differs only in having a dioxymethylene group in place of two methoxyl groups, but the difficulty connected with the supposed synthesis of berberine referred to in last year's Report [68] has led to repetition of the work.[69] This time berberine itself was used as the starting point in place of tetrahydroberberine and the elimination of the dioxymethylene group was effected by the use of hydrochloric acid and phloroglucinol. In this way, the phenolic base (III), in which the two hydroxyl groups replace the dioxymethylene group of berberine, was produced, which on methylation furnished some palmatine (I) and also some jatrorrhizine (II).

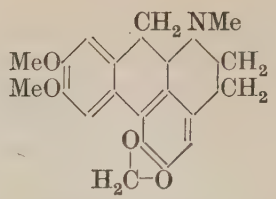


d-Dicentrine, which occurs in *Dicentra* spp. along with protopine, tetrahydropalmatine, and sanguinarine (now believed to be a mixture of chelerythrine and dehydrochelidonine), is regarded by Gadamer [70] as having formula (II) and belonging to the phenanthreno*iso*quinoline group recently re-named the aporphine group (see below). *dl*-Dicentrine has now been synthesised [71] from 1-veratrylhydrohydrastinine by converting this into the 6′-nitro-derivative and diazotising the corresponding 6′-amino-compound (I) in presence of copper powder, a method due to Pschorr.[72] Dicentra therefore contains alkaloids of both the di*iso*quinoline type (protopine and tetrahydropalmatine) and the phenanthreno*iso*quinoline type (dicentrine, chelerythrine, and dehydrochelidonine).

[66] E. Späth and R. Duschinsky, *Ber.*, 1925, **58**, [*B*], p. 1939; *A.*, i, 1313; compare K. Feist and G. L. Dschu, *Arch. Pharm.*, 1925, **263**, 294; *A.*, i, 830.
[67] E. Späth, *Ber.*, 1921, **54**, 3064; *A.*, 1922, i, 166.
[68] *Ann. Reports*, 1924, **21**, 133.
[69] E. Späth and H. Quietensky, *Ber.*, 1925, **58**, [*B*], 2267; *A.*, 1926, **A**, 82.
[70] *Arch. Pharm.*, 1911, **249**, 680; *A.*, 1912, i, 48.
[71] R. D. Haworth, W. H. Perkin, jun., and J. Rankin, *J.*, 1925, **127**, 2018.
[72] *Ber.*, 1904, **37**, 1926; *A.*, 1904, i, 612.

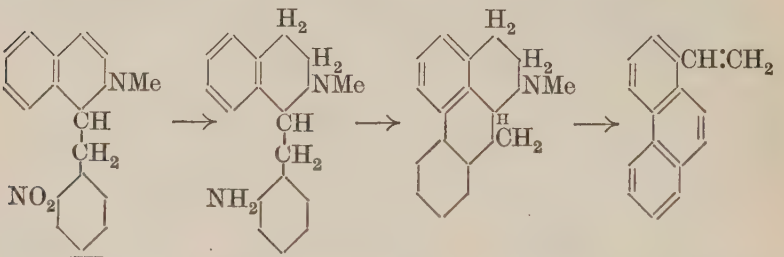


(I.)



(II.)

To the account of the chelidonium alkaloids given last year there is only to be added a reference to the synthesis of aporphine (V), regarded as the parent of the series.[73] For this synthesis, Pschorr's method (see above) was applied to 1-*o*-nitrobenzyl-2-methyl-1 : 2-dihydro*iso*quinoline (III), obtained by condensing *o*-nitrotoluene with the ψ-basic form of *N*-methyl*iso*quinolinium hydroxide. As would be expected, on "exhaustive methylation" aporphine yields 1-vinylphenanthrene (VI) and trimethylamine.



(III.) (IV.) (V.) (VI.)

The most difficult group of the *iso*quinoline alkaloids—morphine, codeine and thebaine—has also received a considerable amount of attention this year,[74] but as this work seems to be still in active progress it may be more convenient to deal with it later.

Among the minor alkaloids of opium it may be mentioned that tritopine [75] has now been shown to be identical with laudanidine. The latter, as was expected, proves to be the *lævo*-form of laudanine.[76]

Indole Derivatives.

It has now been found that indole on complete hydrogenation at 225° in presence of nickel yields *o*-ethyl*cyclo*hexylamine, and not

[73] J. Gadamer, M. Oberlin, and A. Schoeler, *Arch. Pharm.*, 1925, **263**, 81; *A.*, i, 576.

[74] H. Wieland and others, *Annalen*, 1923, **433**, 267; *A.*, 1923, i, 1222; *ibid.*, 1925, **444**, 69; *A.*, i, 1090; *Ber.*, 1925, **58**, [*B*], 2009; *A.*, i, 1448; E. Speyer and others, *Annalen*, 1924, **438**, 34; *A.*, 1925, i, 59; *Ber.*, 1925, **58**, [*B*], 1110, 1113, 1117, 1120, 1125; *A.*, i, 961, 962.

[75] E. Späth and R. Seka, *Ber.*, 1925, **58**, [*B*], 1272; *A.*, i, 1093.

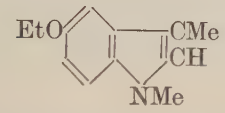
[76] E. Späth and E. Bernhauer, *ibid.*, p. 200; *A.* i, 294.

octahydroindole as previously supposed, but the latter is produced by hydrogenation of indole at atmospheric temperature in presence of spongy platinum.[77] The conclusion previously reached regarding the influence of alkyl substituents is therefore modified and is now stated in the form that the stability of the pyrrolidine ring in dicyclic perhydroindole bases is increased by the presence of alkyl substituents, especially when these are near the nitrogen atom. Thus 2-methylindole yields the octahydro-derivative at 200° and only at 240—250° does scission of the ring occur, producing *o*-propyl-*cyclo*hexylamine. 1 : 2-Dimethylindole gives the fully hydrogenated product even at 240°.[78]

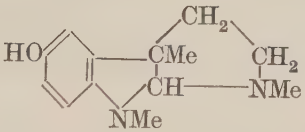
The introduction of a positive cyano-group into the benzene ring of indolecarboxylic acid lowers the reactivity of the hydrogen atoms of the pyrrole ring. Thus the condensation product of 6-cyano-indolecarboxylic acid with aminodimethylacetal yields neither an indolediazine nor a carboline.[79]

The investigation of physostigmine, $C_{15}H_{21}O_2N_3$, the principal alkaloid of Calabar bean, has reached a stage at which a constitutional formula can be assigned to it with a fair degree of certainty.[80a] On hydrolysis, it yields carbon dioxide, methylamine, and eseroline, $C_{13}H_{18}ON_2$, and the latter regenerates physostigmine on treatment with methylcarbimide, so that physostigmine must be the methylcarbamido-derivative of eseroline. The latter furnishes an ethyl ether, eserethole, the methiodide of which on distillation furnishes physostigmol ethyl ether. The latter has been synthesised and shown to be 5-ethoxy-1 : 3-dimethylindole [81] (I). This grouping

(I.)



(II.)



must also be present in eserethole, and with the replacement of EtO– by HO–, in eseroline. The problem of formulating these two resolves itself into ascertaining the manner in which the rest of the molecule (C_3H_7N) is attached. It was already known that the

[77] R. Willstätter, F. Seitz, and J. von Braun, *Ber.*, 1925, **58**, [*B*], 385; *A.*, i, 428; compare *Ann. Reports*, 1924, **21**, 139; and R. Willstätter and D. Jaquet, *ibid.*, 1918, **51**, 767; *A.*, 1918, i, 391.

[78] J. von Braun and O. Bayer, *ibid.*, 1925, **58**, [*B*], 387; *A.*, i, 428.

[79] W. O. Kermack, *J.*, 1924, **125**, 2285; compare *Ann. Reports*, 1924, **21**, 139.

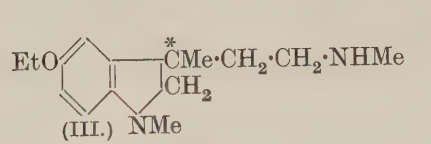
[80a] A. H. Salway, *J.*, 1912, **101**, 978; 1913, **103**, 351.

[81] *Ann. Reports*, 1924, **21**, 143; compare E. Späth and O. Brunner, *Ber.*, 1925, **58**, [*B*], 518; *A.*, i, 574.

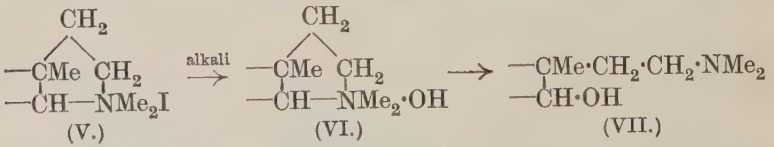
nitrogen atom in this residue was tertiary [80b] and was present as :NMe,[80c] so that the expression can reasonably be extended thus: $-CH_2\cdot CH_2\cdot\dot{N}Me$, which clearly implies a pyrroline ring as in (II) to represent eseroline, whilst physostigmine itself is eseroline with the hydrogen of the hydroxyl group replaced by the methylcarbamido-group, $NHMe\cdot CO\cdot O$.[82]

Eserethole (II with EtO in place of HO) on reduction furnishes dihydroeserethole (III) and with this change a tertiary nitrogen becomes secondary, implying the opening of the pyrroline ring as in (III).

A study of the methylation products of this substance and other allied derivatives led M. Polonovski and M. Polonovski [83a] to



suppose that in eserethole, and consequently in eseroline and physostigmine, the chain beyond the asterisked carbon atom in (III) was unbranched and formed a *N*-methylpiperidine ring as in (IV), which on this view represents eserethole. The ready formation of 5-ethoxy-1 : 3-dimethylindole from eserethole referred to above, however, clearly demonstrates the presence of a methyl group as in (II) at position 3, and these authors have now accepted Stedman and Barger's formula. Further evidence for the latter has been obtained in various ways,[82] for example, when eserethole methiodide (V) is treated with alkali the methohydroxide (VI) first formed undergoes tautomeric modification to eseretholemethine (VII), which is re-converted into the methiodide by hydriodic acid.



The methine on oxidation by potassium ferricyanide or ammoniacal silver nitrate in alcohol, behaves in a manner recalling the

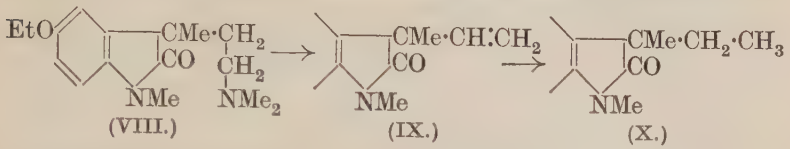
[80b] F. Straus, *Annalen*, 1913, **401**, 350; 1915, **406**, 332; *A.*, 1914, i, 78; 1915, i, 448.

[80c] M. and M. Polonovski, *Bull. Soc. chim.*, 1918, [iv], **23**, 335, 356; 1923, [iv], **33**, 970, 977; *A.*, 1918, i, 504, 505; 1923, i, 940.

[82] E. Stedman and G. Barger, *J.*, 1925, **127**, 247; compare *J.*, 1923, **123**, 758; 1924, **125**, 1373.

[83a] *Bull. Soc. chim.*, 1924, [iv], **35**, 1492; *A.*, 1925, i, 151; compare *A.*, 1924, i, 980, 1093, 1094.

oxidation of 1 : 3 : 3-trimethyl-2-indolinol to the corresponding indolinone,[84] and a compound, to which formula (VIII) is ascribed, is produced. The latter on exhaustive methylation yields trimethyl-



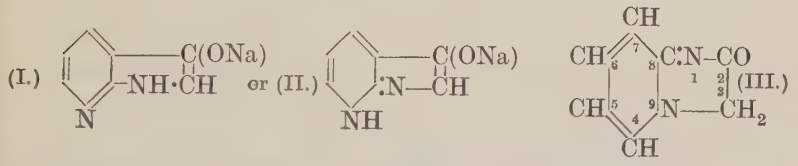
amine, giving the unsaturated substance (IX) which is almost devoid of basic properties, yields a deep red picrate, and on reduction furnishes (X), a substance which it is hoped to synthesise and thus to establish the formula now assigned to physostigmine beyond reasonable doubt. It has since been shown that this formula accounts equally well for the formation of various other series of physostigmine derivatives.[83b]

Glyoxaline Derivatives.

The condensation product of chloroacetic acid and 2-aminopyridine, which was regarded as "pyridylglycine," $NC_5H_4{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$,[85] is now shown to be 2-pyridoneimine-1-acetic acid,

$$CO_2H{\cdot}CH_2{\cdot}N{:}C_5H_4{:}NH,$$

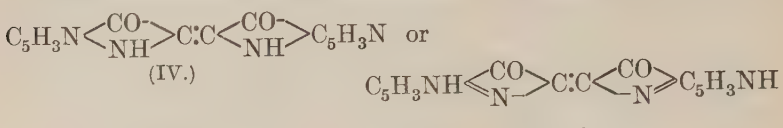
since it is converted by heating into 1-methyl-2-pyridoneimine, $MeN{:}C_5H_4{:}NH$.[86] Similarly the supposed sodium salt of pyrindoxyl (I or II) produced by the action of sodium hydroxide solution on "pyridylglycine" (2-pyridoneimine-1-acetic acid) has been prepared in various other ways, which leave no doubt that it is 2-keto-2 : 3-dihydropyriminazole (III), ring closure having occurred at the N-atom of the pyridine ring, not at carbon atom 3, owing to tautomerism of 2-aminopyridine.



In confirmation of this, it is found that 2-amino-3-methylpyridine, when similarly treated, furnishes 2-keto-7-methyldihydropyriminazole. Oxidation of these dicyclic compounds to the corresponding dyes is effected with a single equivalent of potassium ferricyanide,

[83b] M. and M. Polonovski, *Bull. Soc. chim.*, 1925, [iv], **37**, 744; *A.*, i, 959.
[84] K. Brunner, *Monatsh.*, 1896, **17**, 253; *A.*, 1896, i, 625.
[85] F. Reindel, *Ber.*, 1924, **57**, [*B*], 1381; *A.*, 1924, i, 1235.
[86] A. E. Tschitschibabin, *ibid.*, p. 2092; *A.*, 1925, i, 158; see also this Report, p. 139.

so that Reindel's conception of these products as pyroindigotins (IV) is untenable and the constitution (V) is suggested for them.

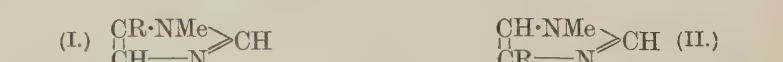


(IV.)

(V.)

Nitration of 2-phenylglyoxaline, like that of 4-phenylglyoxaline,[87] produces predominantly the *p*-compound, the proportions of *p*-, *o*-, and *m*-compounds isolated being 50, 1·5, and 0·2% of the theoretical. The introduction of carboxyl groups progressively diminishes this ratio of *para* to *meta* nitration of the benzene nucleus; thus 2-phenyl-4(or 5)-glyoxalinecarboxylic acid gives a mixture of *p*- and *m*-nitro-compounds, from which by decarboxylation the corresponding *p*- and *m*-nitrophenylglyoxalines are obtained in the ratio 52 : 19 With 2-phenylglyoxaline-4 : 5-dicarboxylic acid this ratio is reversed, the proportion of *p*- to *m*- being 19 : 52.

The study of the methylation of 4(or 5)-R-glyoxalines has now been carried a stage further by the use of diazomethane and of methyl sulphate in presence of aqueous sodium hydroxide.[88] The products formed are the 5 : 1 (I) and 4 :1 (II) -isomerides.



(I.) (II.)

Proportions of 5 : 1- *and* 4 : 1-*isomerides formed.*

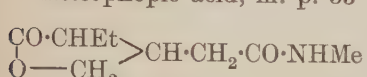
	(a) Me_2SO_4.	(b) Me_2SO_4 + NaOH.	(c) CH_2N_2.
1. R = NO_2	350 : 1	0·33 : 1	45 : 1
2. R = Br	45 : 1	1 : 1	10 : 1
3. R = Ph	0·2 : 1	(not feasible)	0·5 : 1

The results indicate that in each case the more basic isomeride predominates, except when methylation takes place in presence of alkali. Thus in series 1 and 2 [the figures in series 2 refer to 2 : 4-(or 5)-dibromo-5(or 4)-methylglyoxaline] the stronger base is the 5 : 1-isomeride and this is formed almost exclusively in (*a*), predominantly in (*c*), and in equivalence or less with the 4 : 1-isomeride in (*b*) under alkaline conditions. These results correspond with those obtained by Auwers in alkylating indazoles.

[87] F. L. Pyman and E. Stanley, *J.*, 1924, **125**, 2484; compare *Ann. Reports*, 1924, **21**, 148.

[88] W. G. Forsyth and F. L. Pyman, *J.*, 1925, **127**, 573; compare *Ann. Reports*, 1924, **21**, 148, and V. K. Bhagwat and F. L. Pyman, *J.*, 1925, **127**, 1832.

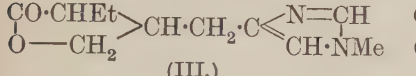
It has been suggested [89] that the isomerism exhibited by pilocarpine and *iso*pilocarpine (IV) is not stereochemical but due to attachment of the side chain in positions 4 and 5, respectively. The methiodides of the two alkaloids, which it is assumed on this view should be identical,[90] are different, but as one is an oil and the other crystalline, making comparison difficult, they were converted into the methochloroplatinates, which are both solid, melt at about the same temperature, but show depression of melting point on admixture. The difference between the two alkaloids must therefore, it is suggested, lie in the nature of the side chain : both yield ozonides, which on decomposition by water furnish different acids, pilocarpine yielding the methylamide of homopilopic acid (I),[89] m. p. 104°, $[\alpha]_{5780}^{15°} + 127{\cdot}7°$, whilst *iso*pilocarpine gives the methylamide of homo*iso*pilopic acid, m. p. 53°, $[\alpha]_{5780}^{15°} + 93{\cdot}9°$.



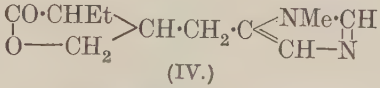
(I.)

(II.)

Another alkaloid of jaborandi leaves, pilocarpidine, has been the subject of two investigations during the year,[91a] the results of which confirm a suggestion made in 1887 [92] that it is the imine corresponding to pilocarpine and is therefore represented by formula II. It is converted by cold methyl iodide into pilocarpine, which, on further methylation and appropriate subsequent treatment, yields pilocarpine methochloroplatinate, identical with that of Langenbeck.[89] Pilocarpidine, on treatment with sodium ethoxide, is converted into *iso*pilocarpidine, and the latter on methylation furnishes *iso*pilocarpine, which, it will be remembered, is also formed by the action of heat or alkalis on pilocarpine. The second investigation [91b] confirms the formation of pilocarpine (IV) from pilocarpidine by methylation, but shows that at the same time an isomeric base, *neo*pilocarpine (III), is formed.



(III.)

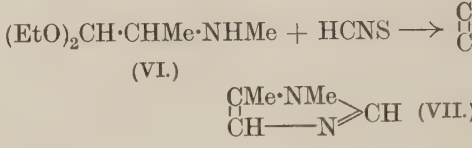


(IV.)

Like pilocarpine, the new isomeride is converted into a stereoisomeric base, *isoneo*pilocarpine, on treatment with alkali. Analytical proof has already been given that in *iso*pilocarpine and probably also in pilocarpine, since the evidence available indicates that these

[89] W. Langenbeck, *Ber.*, 1924, **57**, [*B*], 2072; *A.*, 1925, i, 151.
[90] Compare F. L. Pyman, *J.*, 1910, **97**, 1814.
[91a] E. Späth and E. Kunz, *Ber.*, 1925, **58**, [*B*], 513; *A.*, *i*, 575.
[91b] R. Burtles, F. L. Pyman, and J. Roylance, *J.*, 1925, **127**, 581.
[92] Harnack, *Annalen*, 1887, **238**, 228; compare *A.*, 1886, 85.

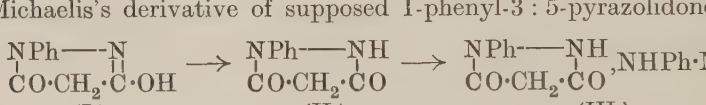
bases are stereoisomerides, the homopilopic complex is attached in position 5 and that the dimethylglyoxaline resulting from its degradation is the 1 : 5- and not the 1 : 4-compound.[93] This view is now confirmed by the synthesis of 1 : 5-dimethylglyoxaline (VII), which results from the oxidation of 2-thiol-1 : 5-dimethylglyoxaline (V), made by the condensation of α-methylaminopropionacetal (VI) with thiocyanic acid.



The 1 : 4-isomeride was also made, but the primary material in this case was not so easily obtained and its preparation gave rise to interesting side reactions.[91b]

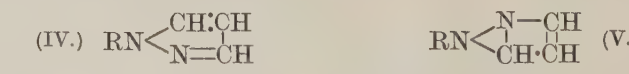
Pyrazole Derivatives.

In the course of an investigation of the action of ketens on hydrazines,[94] a series of 3 : 5-diketopyrazolidines was obtained by the use of carbon suboxide. Thus phenylhydrazine combines with the suboxide to form the unstable substance (I), which, on keeping, changes into the tautomeric phenyl-3 : 5-diketopyrazolidine (II); this yields a phenylhydrazine addition product (III) identical with Michaelis's derivative of supposed 1-phenyl-3 : 5-pyrazolidone.[95]



With nuclear-substituted phenylhydrazines, analogous substances are formed, but in these cases a molecule of phenylhydrazine attaches itself to the substituted diketopyrazolidine formed by means of the β-nitrogen, the products being assigned formulæ of the type (III).

Several long papers have appeared on isomeric relationships in the pyrazole series.[96] In the first of these, it was shown that no evidence could be obtained for the existence of isomeric alkylpyrazoles of types represented by formulæ (IV) and (V), analogous



[93] F. L. Pyman, *J.*, 1922, **121**, 2616; compare H. A. D. Jowett, *ibid.*, 1905, **87**, 794.

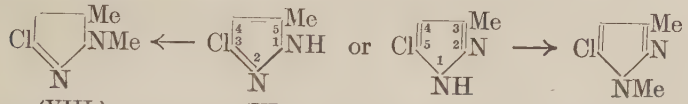
[94] J. van Alphen, *Rec. trav. chim.*, 1924, **43**, 823; *A.*, 1925, i, 80.

[95] *Ber.*, 1892, **25**, 1502; *A.*, 1892, i, 1004.

[96] K. von Auwers and others, *ibid.*, 1922, **55**, [*B*], 3880; 1925, **58**, [*B*], 528; *A.*, 1923, i, 151; 1925, i, 585; *J. pr. Chem.*, 1925, [ii], **110**, 153, 204, 235; *A.*, i, 1176, 1178, 1180.

with those found in the indazoles,[97] and that it was improbable that the 3- and 5-derivatives of pyrazole were identical, as had been assumed by Knorr and others. The formation of 1 : 3-derivatives in cases where 1 : 5-derivatives would be expected, as in the oxidation of 1 : 5-dimethylpyrazolidine, is assumed to be due to the instability of the latter. The 1 : 5-dialkylpyrazoles appear to be incapable of existence, but 3- and 5-phenyl-1-alkylpyrazoles have now been prepared.

It has been suggested that the instability of the 1 : 5-dialkyl derivatives is due to mutual repulsion of electrochemically similar groups, but the experimental results indicate that this explanation is inadequate. Rojahn's preparation of 3-chloro-1 : 5-dimethylpyrazole, by the action of methyl iodide on the sodium salt of 5-chloro-3-methylpyrazole,[98] appeared to negative the view that the 1 : 5-dialkyl derivatives are unstable, and this reaction has been fully investigated. 5-Chloro-3-methylpyrazole, formed from 3-methylpyrazol-5-one by the action of phosphoryl chloride, may have either formula (VI) or (VII). On methylation, it can furnish either 3-chloro-1 : 5-dimethylpyrazole (VIII) alone, or a mixture of this with 5-chloro-1 : 3-dimethylpyrazole (IX), depending on the methylating agent used and the conditions observed.[99]

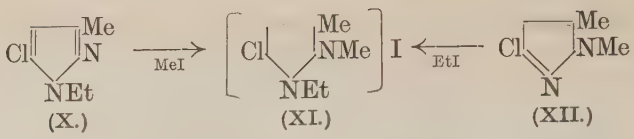


(VIII.) (VI.) (VII.) (IX.)

Both chlorodimethyl derivatives yield the same 5-chloro-1 : 2 : 3-trimethylpyrazolium iodide (type XI) with methyl iodide, and this quaternary salt on heating yields the 1 : 5-dimethyl derivative (type VIII), the methyl group at position 2 being eliminated as methyl iodide.

Similarly, when 5-chloro-3-methylpyrazole is treated with ethyl bromide in alcoholic sodium ethoxide, the tri-substituted pyrazoles formed are Cl : Me : Et = 5 : 3 : 1 and Cl : Me : Et = 3 : 5 : 1. If these in turn are treated again with methyl iodide, the products are mixtures of isomerides in which Cl : Me : Me : Et = 5 : 2 : 3 : 1 and 3 : 2 : 5 : 1. The same tetra-substituted products are formed by the action of ethyl iodide on the two 5 or 3-chloro-2 : 3- or 2 : 5-dimethylpyrazoles, so that the formation of these quaternary salts is formulated thus, the iodine atom being regarded as ionically attached to the whole molecule and not specifically to either nitrogen atom :

[97] *Ann. Reports*, 1924, **21**, 150.
[98] *Ber.*, 1922, **55**, [*B*], 2959; *A.*, 1922, *i*, 1183.
[99] Compare this Report, p. 156.



(X.) (XI.) (XII.)

When heated, these quaternary pyrazolium salts are decomposed into pyrazoles and alkyl halides, the alkyl group being in preference lost from the nitrogen contiguous to the chlorine atom,[1] unless the other alkyl group possesses weak affinity, for example, benzyl or allyl: thus, 5-chloro-2-benzyl-1 : 3-dimethylpyrazolium iodide yields benzyl iodide and 3-chloro-1 : 5-dimethylpyrazole, whilst 5-chloro-1 : 3-dimethyl-2-ethylpyrazolium iodide furnishes 3-chloro-5-methyl-1-ethylpyrazole.

It is clear, therefore, that the presence of a chlorine atom greatly increases the stability of the 1 : 5-dialkyl derivatives, which are actually more stable than the 5-chloro-1 : 3-dialkylpyrazoles.

The later papers deal with a similar investigation of the influence on stability of the replacement of the 3(or 5)-methyl group by phenyl and with the *N*-alkyl and *N*-acyl derivatives of methylpyrazoles.

In a study of the conditions under which phenylhydrazones of unsaturated compounds pass into pyrazolines, it is pointed out that whilst unsaturated ketones generally give pyrazolines directly, unsaturated aldehydes furnish phenylhydrazones, which may be isomerised to pyrazolines. The presence of the *p*-nitro-group in phenylhydrazine tends to inhibit the formation of pyrazolines, whilst methylhydrazine favours it. Colour reactions are inadequate means of distinguishing between phenylhydrazones and pyrazolines, and reduction to the corresponding aniline, or hydrolysis by mixed acetic and sulphuric acids, is suggested instead for the simple, and substituted phenylhydrazones, respectively.[2]

When pyrazolines are treated with potassium cyanate in acetic acid solution, the corresponding carbamides, *e.g.*, 3 : 5 : 5-trimethylpyrazoline-1-carbamide (I), are formed.[3] These compounds are weak bases, yield well-crystallised picrates, and with acids regenerate the original pyrazolines. The by-product obtained in the action of semicarbazide on mesityl oxide [4] no doubt belongs to this type.

It is interesting to note that the pyrazoline obtained as a degrad-

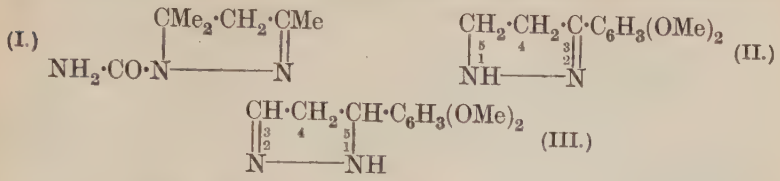
[1] Compare *Ann. Reports*, 1924, **21**, 147, 148, refs. 91, 92, 93.

[2] K. von Auwers and A. Kreuder, *Ber.*, 1925, **58**, [*B*], 1974; *A.*, i, 1454; compare *ibid.*, 1909, **42**, 4411; *A.*, 1910, i, 70.

[3] R. Locquin and R. Heilmann, *Compt. rend.*, 1925, **180**, 1757; *A.*, i, 837.

[4] M. Scholtz, *Ber.*, 1896, **29**, 610; *A.*, 1896, i, 343; compare C. Harries and F. Kaiser, *ibid.*, 1899, **32**, 1338; *A.*, 1899, i, 637; H. Rupe and S. Kessler, *ibid.*, 1909, **42**, 4503, 4715; *A.*, 1910, i, 15, 93.

ation product of catechin has now been synthesised and shown to have the constitution (II), although the product first formed is



probably represented by (III).[5] This possibility has led to an investigation of the chances of such Δ-isomerism among these compounds. Although Buchner and Heide have recorded such cases for methyl ethyl 4-phenylpyrazoline-3 : 5-dicarboxylates, they could obtain from these only one 3-phenylpyrazoline (type II) by methods which would be expected to yield Δ-isomerides, and in the present instance all attempts to prepare such isomerides failed so far as 3-arylpyrazolines were concerned. On the other hand, two 3 : 5-anisylphenylpyrazolines (types II and III) and their 4-hydroxy-derivatives have been obtained, and also two 3 : 5-phenylmethylpyrazolines and distinct 3- and 5-methylpyrazolines, but attempts to prepare pyrazolines containing the double linking between carbon atoms 3 and 4 or 4 and 5 failed.

Indazole Derivatives.

The synthesis of tetrahydroindazoles from *cyclo*hexanone referred to last year [6] has been extended to mono- and di-methyl*cyclo*hexanones and it has been found that a methyl group in the ortho-position to carbonyl favours the formation of 2-alkylindazoles; in the para-position it exerts no directive influence, whilst two methyl groups in the meta-position to carbonyl favours the production of 1-alkylindazoles. With phenyl in place of methyl groups, the differences in orienting effect are less distinct.[7]

Although it has been possible to prepare a number of indazoles by the method of Reich and Gaigailian,[8] *viz.*, the action of sodium hydroxide on substituted hydrazones of 2 : 6-dinitrobenzaldehyde, all attempts to use it for the preparation of 1-acylindazoles failed.[9]

The compound obtained by heating *o*-aminobenzhydrazide in presence of quinoline at 200° has been regarded as (*a*) 3-hydroxy-

[5] K. Freudenberg and others, *Annalen*, 1924, **440**, 36, 38; *A.*, 1925, i, 69, 70.

[6] *Ann. Reports*, 1924, **21**, 149.

[7] K. von Auwers, L. von Sass, and W. Wittekindt, *Annalen*, 1925, **444**, 195; *A.*, i, 1181; compare *ibid.*, 1925, **441**, 68; *A.*, i, 310.

[8] *Ber.*, 1913, **46**, 2380; *A.*, 1913, i, 995.

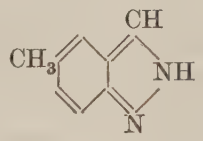
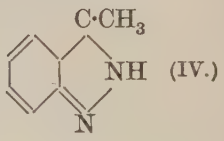
[9] K. von Auwers and E. Frese, *Ber.*, 1925, **58**, [*B*], 1369.

indazole [10] and (*b*) benz*iso*pyrazolone.[11] Further investigation shows that it is bimolecular and is to be regarded as di-3-hydroxyindazole (I).[12] 3-Cyano-2-phenylindazole-1-oxide (II) has been prepared by

(I.) $\begin{matrix} C_6H_4\cdot C(OH)\cdot N\cdot NH \\ NH-N\cdot (OH)C\cdot C_6H_4 \end{matrix}$ $C_6H_4 \begin{matrix} N(:O) \\ C(CN) \end{matrix} > NPh$ (II.)

the action of aniline on *o*-nitromandelonitrile in alcohol in presence of sodium acetate.[13]

The alkylation of 3- and 5-methylindazoles has been investigated [14] to see whether they behave like the simple pyrazoles [15] and the tetrahydroindazoles.[16] 5-Methylindazole (III) behaves exactly like

(III.)  (IV.) 

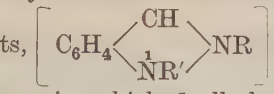
the latter in giving 1- or 2- or both alkyl derivatives, depending on the reagent used and the experimental conditions, and that is also true of the 5-methylindazole-2-carboxylates. 3-Methylindazole (IV), on the contrary, shows some difference between the behaviour of free alkylpyrazole and alkylpyrazole forming part of an indazole complex. In 3-methylindazole, for example, the methyl group appears to exert scarcely any directing influence in benzylation, mixtures of 1- and 2-benzyl-3-methylindazoles being formed, with the latter usually predominating. The *o*- and *p*-nitrobenzoyl derivatives of 3-methylindazole (IV) exist in both stable and labile forms. The introduction of a bromine atom at position 3 in 5-methylindazole scarcely affects the course of subsequent methylation. The 3 : 5-dibromo-1 : 2-dimethylindazolium bromide on heating yields 3 : 5-dibromo-1-methylindazole exclusively, whilst the corresponding 5 : 7-dibromo-compound furnishes a mixture of the 1-methyl and 2-methyl derivatives. The introduction of halogen in the benzene ring of indazole reduces the basic character; thus 5 : 7-dibromoindazole no longer forms a picrate and is soluble in alkalis, whilst the 3 : 5 : 7-tribromoindazole is definitely acid in character. In general, the 3-halogenated indazoles are more acid than basic.

The question of the constitution of the labile and stable forms of

[10] G. Heller and W. Köhler, *Ber.*, 1923, **56**, [*B*], 1595; *A.*, 1923, i, 850.
[11] C. Thode, *J. pr. Chem.*, 1904, [ii], **69**, 92; *A.*, 1904, i, 347.
[12] A. Hantzsch, *Ber.*, 1925, **58**, [*B*], 680; *A.*, i, 702.
[13] G. Heller and G. Spielmeyer, *ibid.*, p. 834; *A.*, i, 838.
[14] K. von Auwers and A. Lohr, *J. pr. Chem.*, 1924, [ii], **108**, 297; *A.*, 1925, i, 73.
[15] Compare this Report, p. 159. [16] *Ann. Reports*, 1924, **21**, 150.

acylindazoles is simplified [16] by the admission that many of the compounds previously described as " stable 2-acylindazoles " may be acyl-1-indazoles, since the labile 2-toluenesulphonylindazoles readily pass into the stable 1-derivatives. This reduces the number of isomerides from three to two and renders the assumption of stereoisomerism unnecessary: the spectrochemical behaviour of the two forms supports the view that they are structural isomerides. The formation of 2-acylindazoles, by the action of acyl chlorides on indazoles at low temperatures, or on the silver salt, is now represented as taking place thus:

whilst with the sodium salts the strongly electropositive metallic atom reacts directly with the chlorine of the acyl chloride, so that 1-acyl compounds are produced directly.[17]

In the present Report several examples of the thermal decomposition of the quaternary salts derived from pyrazole and indazole have been given [18] and this reaction has been used to determine the relative tenacity with which radicals are attached to nitrogen in indazolium salts,  X, by measurement of the relative proportions in which 1-alkyl- and 2-alkyl-indazoles are formed.[19] When R′ = Me and R is represented by various alkyl groups, the tenacity with which R is held increases from methyl to propyl or *iso*propyl and then diminishes: allyl, benzyl and substituted benzyl groups are held less firmly than the methyl group, and the same order is generally maintained for the same groups in position 1. These results only differ from those arrived at by von Braun [20] by other methods, as regards the position of the *n*-butyl radical and the equivalence of the propyl and the *iso*propyl group.

Oxazoles and iso*Oxazoles.*

The observation that chlorinated compounds are formed by the interaction of epichlorohydrin and sodium cyanamide has necessitated a revision of views previously published as to the course of the reaction between ethylene chlorohydrin and sodium cyanamide.[21] The first change is the hydrolysis of disodium cyanamide,

[17] K. von Auwers, *Ber.*, 1925, **58**, [*B*], 2081; *A.*, i, 1460.

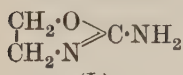
[18] This Report, pp. 160, 162.

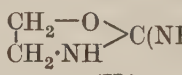
[19] K. von Auwers and W. Pfuhl, *Ber.*, 1925, **58**, [*B*], 1360; *A.*, i, 1100.

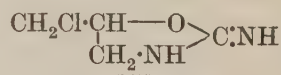
[20] J. von Braun and J Weismantel, *ibid.*, 1922, **55**, [*B*], 3165; *A.*, 1922, i, 1150.

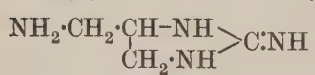
[21] E. Fromm and others, *Annalen*, 1925, **442**, 130; *A.*, i, 594; compare *A.*, 1922, i, 529.

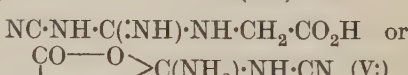
$NC{\cdot}NNa_2$, to the monosodium salt, $NC{\cdot}NHNa$, and sodium hydroxide, followed by the formation of ethylene oxide, which combines with the monosodium salt to form an alcoholate, which is at once hydrolysed to 2-amino-oxazoline (cyanamidoethyl alcohol) (I, in which $\cdot N{:}C{\cdot}NH_2$ may also act as $\cdot NH{\cdot}C{:}NH$) already known.[22] The latter reacts with ammonium chloride to form 2 : 2-diamino-oxazoline (guanidoethyl alcohol; II). Epichlorohydrin with sodium cyanamide gives 2-imino-5-chloromethyloxazolidine (III); the latter is converted by ammonia into a substance, which is probably 2-amino-5-aminomethyliminazoline (IV). With chloroacetic acid sodium cyanamide yields as the main product dicyanodiamidoacetic acid (cyanoguanidoacetic acid), which can react in either of the two forms shown (V).


(I.)

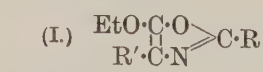

(II.)

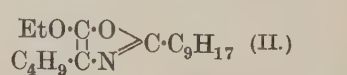

(III.)


(IV.)


(V.)

A series of compounds of type 1 has been prepared by the dehydration of amino-acids, usually with phosphorus pentachloride.[23] Closure of the ring becomes more difficult as the weight of the acyl residue increases; thus in the case of the acylglycine esters, $R{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et$ or $R{\cdot}CO{\cdot}NH{\cdot}CHR'{\cdot}CO_2Et$, the ethyl ester of *iso*valerylglycine yields 5-ethoxy-2-*iso*butyloxazole (I; $R = C_4H_9$), but that of *n*-hexoylglycine gives only a trace of oxazole, whilst those of *n*-octoylglycine and its higher homologues remain unattacked. The ethyl ester of *d*-α-methyl-*n*-butyryl-*l*-leucine yields the optically active 5-ethoxy-4-*iso*propyl-2-*sec.*-butyloxazole, but this on hydrolysis furnishes an inactive leucine. The hope that an active amino-acid might be obtained in the hydrolysis in presence of a second asymmetric carbon atom in the substituent acyl group was not realised.


(I.)

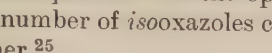

(II.)

Thus hydrolysis of 5-ethoxy-2-1′ : 2′ : 2′ : 4′-tetramethyl*cyclo*pentyl-4-*iso*butyloxazole (II), in which the groups C_4H_9 and C_9H_{17} are both optically active, furnished only inactive leucine and *d*-campholyl-*dl*-leucine.

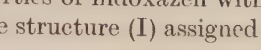
[22] S. Gabriel, *Ber.*, 1889, **22**, 1139; *A.*, 1889, i, 848.

[23] P. Karrer and others, *Helv. Chim. Acta*, 1924, **7**, 763; 1925, **8**, 203, 205; C. Granacher, *ibid.*, 1925, **8**, 211; *A.*, 1924, i, 1118; 1925, i, 594.

A comparison [24] of the optical properties of indoxazen with those of a number of *iso*oxazoles confirms the structure (I) assigned to the former.[25]



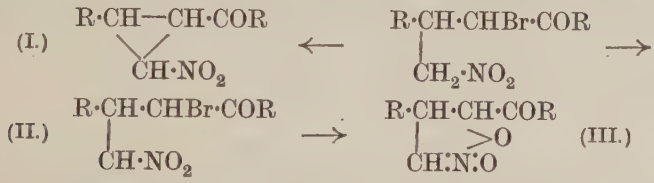
(I.)



(II.)

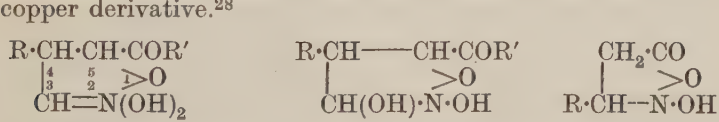
An interesting series of *iso*oxazoles has been prepared by the action of hydroxylamine on substituted thioamides of ethyl acetylmalonate.[26] A typical example is 3-anilino-5-keto*iso*oxazole (II), formed by treating the additive compound of ethyl acetylmalonate and phenylthiocarbimide with hydroxylamine. With hydrazine, a similar series of pyrazoles is formed.

The small yields obtained in reactions used for the preparation of *cyclo*propane derivatives, having a nitro-group attached to one of the carbon atoms of the ring (I), is due to secondary reactions in which hydrogen bromide is eliminated from the *aci*-form (II) of the nitro-compound, resulting in the formation of *iso*oxazoline oxides,[27] which are represented by formula III, or its tautomeric



(I.) (II.) (III.)

form in which the oxygen is held between the nitrogen atom and carbon atom 3 thus, , (III) being preferred. These oxides combine with water, alcohols, ammonia, and amines, forming compounds which are all similar in type and are represented, in the case of the water additive product, by formula (IV) or (V), of which (V) is preferred on account of its similarity to that of a known hydroxy-*iso*oxazolidone (VI), which, like these addition compounds, forms a copper derivative.[28]



(IV.) (V.) (VI.)

In later work, phenylated derivatives of these *iso*oxazoline oxides

[24] K. von Auwers, *Ber.*, 1924, **57**, [*B*], 461; *A.*, 1924, i, 572.

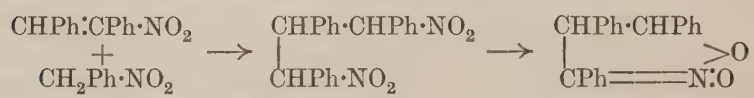
[25] A. Conduché, *Ann. Chim. Phys.*, 1908, [iii], **13**, 5; *A.*, 1908, i, 154.

[26] D. E. Worrall, *J. Amer. Chem. Soc.*, 1922, **44**, 1551; 1923, **45**, 3092; 1924, **46**, 2832; *A.*, 1922, i, 874; 1924, i, 208; 1925, i, 308.

[27] E. P. Kohler, *ibid.*, 1924, **46**, 503, 1733, 2105; *A.*, 1924, i, 571, 998, 1239.

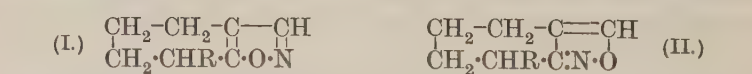
[28] T. Posner, *Ber.*, 1906, **39**, 3515; *A.*, 1907, i, 55.

were prepared, which are represented by the same type of formula, although they differ considerably in properties from the original compounds; thus they are not ruptured by strong bases, form no additive compounds with water, etc., do not yield insoluble copper derivatives, and are dehydrated instead of being acylated by acid chlorides and anhydrides. These differences are ascribed to the absence of the labile hydrogen atom in position 3 as in 5-benzoyl-3 : 4-diphenyl*iso*oxazoline oxide (compare IV for numbers). 3 : 4 : 5-Triphenyl*iso*oxazoline oxide is obtained by the condensation of nitrostilbene with phenylnitromethane in presence of sodium methoxide, probably according to the following scheme :



This product contains no reactive group except the system $\cdot\dot{C}=\dot{N}:O$ characteristic of these compounds. It is readily converted into triphenyl*iso*oxazole [29] by boiling with aqueous-alcoholic sodium hydroxide, and this " stripping " by the alkali is no doubt the source of the same *iso*oxazole, which is the chief by-product of the reaction in which the oxide is formed. This oxide again differs markedly in its reactions from those previously described. Reduction with zinc and acetic acid converts it into 2-hydroxy-3 : 4 : 5-triphenyl*iso*-oxazoline, which is also obtained by the action of magnesium ethyl bromide on the oxide. With phosphorus pentachloride the oxide behaves like diphenylfuroxan [30] (diphenyl*iso*oxadiazole), oxygen being lost and triphenyl*iso*oxazoline formed.

The condensation of 2-hydroxymethylene*cyclo*hexanone with hydroxylamine hydrochloride gives a mixture of the two isomeric tetrahydrobenz*iso*oxazoles [31] of types I and II (R = H), the 4 : 5-compound (type I) predominating always and in presence of



hydrochloric acid forming 85% of the product. 6-Methyl-2-hydroxymethylene*cyclo*hexanone behaves similarly, and in this case attempts to increase the yield of the 3 : 4-product (type II) by the use of 2-ethoxymethylene*cyclo*hexanone gave a mixture of products (III and IV). In neutral solution the free hydroxymethylene

[29] Compare J. Meisenheimer and K. Weibezahn, *Ber.*, 1921, **54**, [*B*], 3195; *A.*, 1922, i, 176.

[30] H. Wieland and L. Semper, *Annalen*, 1907, **358**, 36; *A.*, 1908, i, 108.

[31] K. von Auwers, T. Bahr, and E. Frese, *Annalen*, 1925, **441**, 54; *A.*, i, 308.

$$\begin{array}{l} CH_2{-}CH_2{-}CH{\cdot}CH{:}NOH \\ CH_2{\cdot}CHMe{\cdot}CO \end{array} \qquad \begin{array}{l} CH_2{-}CH_2{-}C{\cdot}CH{:}NOH \\ CH_2{\cdot}CHMe{\cdot}C{\cdot}OH \end{array} \qquad \begin{array}{l} CH_2{-}CH_2{-}C{\cdot}CN \\ CH_2{\cdot}CHR{\cdot}C{\cdot}ONa \end{array}$$

(III.) (IV.) (V.)

ketone also yields (IV), which readily loses water and forms the 4 : 5-*iso*oxazole (I). The course of the reaction therefore appears to be

$$\begin{array}{l} -C{:}CH{\cdot}OR' \\ -CO \end{array} \longrightarrow \begin{array}{l} -CH{\cdot}CH(OR'){\cdot}NH{\cdot}OH \\ -CO \end{array} \longrightarrow$$

$$\begin{array}{l} -CH{\cdot}C{\cdot}NH{\cdot}OH \\ -CO \end{array} \longrightarrow \text{(III and IV)} \longrightarrow \text{(I.)}$$

All four substances are volatile liquids and the tetrahydrobenz-*iso*oxazoles (I and II) closely resemble the corresponding dialkyl-*iso*oxazoles. The 4 : 5-compounds (I) are decomposed in the cold by sodium methoxide, giving the enolic forms of the cyanoketones (V), which yield oximes readily convertible by traces of alkali into *C*-aminotetrahydrobenz*iso*oxazoles, except in the case of 2-cyano-2-alkyl*cyclo*hexanones.[32]

T. A. Henry.

[32] K. von Auwers, T. Bahr, and E. Frese, *Annalen*, 1925, **441**, 68; *A.*, i, 310.

ANALYTICAL CHEMISTRY.

THERE is no record during the year of any advance in analytical methods of an entirely novel character. As is usually the case, the publications generally deal with improvements in well-known processes and applications to special problems. Certain attempts to apply the methods of *X*-ray analysis beyond the rare earths have been recorded, and it seems not unlikely that progress in this direction may furnish another method of general utility. The limitations of various indicators have been the subject of further inquiry and several applications of electrometric titration have likewise been communicated, further demonstrating the elegance of this method when properly applied. New apparatus and microchemical methods of analysis are not dealt with in this Report, because they are not sufficiently numerous or important to call for special attention on this occasion.

Inorganic Analysis.

Qualitative.—A series of reactions, carried out on a drop of solution, has been devised for the qualitative analysis of solutions containing the nitrates of most of the metals of the first three groups; in another scheme, a preliminary separation into groups is carried out by treating the precipitated sulphides of all the metals with acids of different concentration.[1] In this connexion, the interesting study on the behaviour of precipitated sulphides of the heavy metals is of importance. When nickel sulphide is precipitated together with lead sulphide, it is appreciably soluble in 1 : 10 hydrochloric acid, whereas its solubility in acid when precipitated alone is small. Digestion with acetic acid of a mixture of coprecipitated zinc and manganese sulphides fails to dissolve all the manganese. From among other examples given in the study may be cited the fact that the ordinary hydrogen sulphide method fails to effect a complete separation of mercury from zinc and cadmium and of tin from cobalt.[2]

Characteristic precipitates are given by copper in neutral solution with thiocyanate and tolidine and with iodide and benzidine;[3]

[1] N. A. Tananaev, *Z. anorg. Chem.*, 1924, **140**, 320; *A.*, 1925, ii, 324.
[2] F. Feigl, *Z. anal. Chem.*, 1924, **65**, 25; *A.*, 1925, ii, 70.
[3] G. Spacu, *ibid.*, 1925, **67**, 31; *A.*, ii, 1003.

the formation of a deep violet coloration due to copper bromide may be used as a sensitive reaction for either of these ions.[4] Traces of gold may be detected by the alteration in colour of a silver sol produced from silver nitrate, metol, and sodium sulphite.[5]

Basic bismuth nitrate has been applied to the removal of phosphates and of oxalates;[6] zirconium oxychloride has also been used in the case of phosphates.[7] The method sometimes adopted of eliminating phosphoric acid by heating the precipitated phosphates with sodium carbonate is completely successful only in the case of iron and barium.[8]

Aluminium salts in neutral solution yield a characteristic green fluorescence with solutions of morin or of morinsulphonic acid, and it is claimed that the test is of great delicacy.[9] In the absence of ferric iron, the formation of a crimson lake with aurintricarboxylic acid, insoluble in ammonia containing ammonium carbonate (by which interfering "lakes" from chromium and the alkaline earths are removed), indicates the presence of aluminium.[10]

A delicate test for cobalt depends on the formation of a blue precipitate with sodium silicate, soluble in excess of the reagent, the pale green precipitate given by nickel under the same conditions being insoluble.[11]

The characteristic precipitates or colorations given by solutions of copper, iron, and cobalt salts with dinitrosoresorcinol have been employed as sensitive tests for these metals.[12]

Sodium oxalate is less soluble in a saturated solution of ammonium oxalate than in water, and this fact has been utilised for the detection of sodium.[13] Alternatively, enough alcohol must be added to the aqueous solution to produce a concentration of 30% alcohol by volume.[14] A filter dyed with crystal-violet is stated to be superior to blue glass in the flame test for potassium.[15]

The intense red colour produced when sodium chloro-osmate is

[4] K. Scheringa, *Pharm. Weekblad*, 1925, **62**, 173; *A.*, ii, 326.

[5] A. Steigmann, *Chem. Ztg.*, 1925, **49**, 423; *A.*, ii, 719.

[6] A. Keschan, *Z. anal. Chem.*, 1925, **65**, 346; **67**, 81; *A.*, ii, 328, 1008.

[7] L. J. Curtman, C. Margulies, and W. Plechner, *Chem. News*, 1924, **129**, 299, 315; *A.*, 1925, ii, 68.

[8] A. Colani, *Bull. Soc. chim.*, 1925, [iv], **37**, 937; *A.*, ii, 1001.

[9] E. Schantl, *Mikrochem.*, 1924, **2**, 174; *A.*, 1925, ii, 440.

[10] L. P. Hammett and C. T. Sottery, *J. Amer. Chem. Soc.*, 1925, **47**, 142; *A.*, ii, 601.

[11] S. J. Tindal, *Chem. News*, 1925, **130**, 34; *A.*, ii, 242.

[12] M. L. Nichols and S. R. Cooper, *J. Amer. Chem. Soc.*, 1925, **47**, 1268; *A.*, ii, 715.

[13] J. Meyerfeld, *Z. anal. Chem.*, 1925, **67**, 150; *A.*, ii, 1202.

[14] L. W. Winkler, *Pharm. Zentr.*, 1925, **66**, 669; *A.*, ii, 1095.

[15] J. Meyer, *Helv. Chim. Acta*, 1925 **8**, 146; *A.*, ii, 601.

boiled with thiocarbamide in the presence of a little hydrochloric acid may be used as a test for osmium, the test being sensitive to 1 part in 100,000.[16]

Colour reactions of nitrates and nitrites with various organic compounds are described.[17] The nitrate and perchlorate of α-phenyl-β-diethylaminoethyl *p*-nitrobenzoate, whilst too soluble to be of value for gravimetric determination of the anions, are available for their qualitative detection.[18] A study has been made of the delicacy of the ferrous sulphate test for nitrate and nitrite and the diphenylamine reaction; [19] and a test for nitrate is described based on reduction to nitrite by metallic lead, any nitrite originally present being removed by appropriate means.[20]

Ammonia may be detected in the presence of and removed from a solution of an aliphatic amine salt by precipitation with sodium cobaltinitrite and sodium nitrite.[21]

Quantitative.—Borax has been found to be suitable as a standardising reagent, both for acids and for bases, the indicators of appropriate p_H range being methyl-orange and phenolphthalein, respectively.[22] Aminosulphonic acid [23] and *p*-nitrobenzoic acid [24] are other suggested standards.

The mixture in equal proportions of neutral-red and phenol-red gives a sharp colour change at the point of real neutrality at p_H 7·07.[25] A detailed investigation of the influence of alcohol, salts, and temperature on the change point of dimethyl-yellow, bromophenol-blue, and phenolphthalein has been made.[26] Potassium ferritri-pyrocatechol-oxide is an indicator similar in many respects to phenolphthalein in its behaviour. The colour change is due to an alteration in the complex anion.[27]

Chloramine T behaves like an inorganic hypochlorite, but is much more stable, so that with the addition of a small amount of

[16] L. Tschughaev, *Z. anorg. Chem.*, 1925, **148**, 65; *A.*, i, 1395.

[17] S. Vági, *Z. anal. Chem.*, 1925, **66**, 14, 101; *A.*, ii, 599; A. Novelli, *Anal. Asoc. Quím. Argentina*, 1925, **13**, 13; *A.*, ii, 900; L. Ekkert, *Pharm. Zentr.*, 1925, **66**, 733; *A.*, ii, 1200.

[18] C. S. Marvel and V. du Vigneaud, *J. Amer. Chem. Soc.*, 1924, **46**, 2661; *A.*, 1925, ii, 240.

[19] F. L. Hahn and G. Jaeger, *Ber.*, 1925, **58**, [*B*], 2340; *A.*, ii, 1199.

[20] *Ibid.*, p. 2335; *A.*, ii, 1199.

[21] P. Leone, *Gazzetta*, 1925, **55**, 246; *A.*, ii, 907.

[22] M. G. Mellon and V. M. Morris, *Ind. Eng. Chem.*, 1925, **17**, 145; *A.*, ii, 325.

[23] L. Herboth, *Arch. Pharm.*, 1924, **262**, 517; *A.*, 1925, ii, 155.

[24] W. M. Thornton, jun., and D. Getz, *Amer. J. Sci.*, 1925, [v], **9**, 176; *A.*, ii, 597.

[25] G. Chabot, *Bull. Soc. chim. Belg.*, 1925, **34**, 202; *A.*, ii, 899.

[26] A. Richter, *Z. anal. Chem.*, 1924, **65**, 209; *A.*, 1925, ii, 237.

[27] K. Binder, *ibid.*, 1925, **66**, 1; *A.*, ii, 596.

potassium iodide and starch as indicator, it can replace iodine in most analytical processes.[28]

When standardising thiosulphate solutions, considerable economy in potassium iodide may be secured by using a slight excess of potassium iodate over the amount required to produce sufficient iodine, a small crystal of the iodide, and titrating very slowly. This method would appear to be advantageous when large quantities of thiosulphate solutions are used.[29] Hydrazine sulphate is proposed as a more satisfactory standard for iodometry than thiosulphate,[30] whilst the conditions necessary for the accurate standardisation of thiosulphate solutions against iodine or potassium permanganate, dichromate or bromate are discussed in detail.[31] Attention is again directed to the greater delicacy obtainable by the use of liquids such as benzene and carbon tetrachloride in the place of starch.[32] Methods depending upon the formation of cyanogen iodide are applied to the determination of numerous types of substances, such as hydrazine, hydrogen peroxide, and cyanides.[33]

Bromine solutions in *N*-potassium bromide are the most suitable for general use for volumetric work. Applications of this reagent and of hypobromite to the determination of iron, tin, and other substances are described.[34]

Reduction with liquid lead amalgam followed by titration with permanganate has been applied to ferric and uranyl salts, to tungstic, titanic, and molybdic acids, and to the determination of phosphorus by reduction of the molybdenum in ammonium phosphomolybdate.[35]

A rapid method of determining metals in mercury is based on the fact that all metals more electropositive than mercury, except cobalt, pass rapidly into solution as sulphates when their amalgams are shaken with permanganate in dilute sulphuric acid; the end-point is indicated by the breaking of the surface of the mercury into bubbles.[36]

[28] A. Noll, *Chem. Ztg.*, 1924, **48**, 845; *A.*, 1925, ii, 66.

[29] M. Dimitrov, *Z. anorg. Chem.*, 1924, **136**, 189; *A.*, 1925, ii, 598.

[30] E. Cattelain, *J. Pharm. Chim.*, 1925, [viii], **2**, 387; *A.*, ii, 1197.

[31] S. Popov and J. L. Whitman, *J. Amer. Chem. Soc.*, 1925, **47**, 2259; *A.*, ii, 1093.

[32] N. Kanô, *Sci. Rep. Tôhoku Imp. Univ.*, 1925, **14**, 101; *A.*, ii, 1010; I. M. Kolthoff, *Pharm. Weekblad*, 1925, **62**, 878; *A.*, ii, 1000.

[33] R. Lang, *Z. anorg. Chem.*, 1925, **142**, 229, 280; **144**, 75; *A.*, ii, 713.

[34] W. Manchot and F. Oberhauser, *ibid.*, 1924, **139**, 40; *A.*, 1925, ii, 161; F. Oberhauser, *ibid.*, 1925, **144**, 257; *A.*, ii, 828; R. Lang, *Z. anal. Chem.*, 1925, **67**, 1; *A.*, ii, 1009.

[35] K. Someya, *Z. anorg. Chem.*, 1925, **145**, 168; **148**, 58; *A.*, ii, 904, 1201.

[36] A. S. Russell and D. C. Evans, *J.*, 1925, **127**, 2221.

The reaction between sodium hydroxide and solutions of a number of metals has been followed electrometrically by the hydrogen and oxygen electrodes, and the possibility of graded precipitation of hydroxides is discussed in detail.[37]

The pyridine–thiocyanate precipitation of copper has been applied to the separation of this element from mercury.[38] Ethyl acetonedioxalate may be utilised for the separation of copper, especially in small quantities, from cadmium and zinc.[39] For the quantitative conversion of cupric sulphide into cuprous sulphide, it is claimed that heating in an atmosphere of hydrogen and hydrogen sulphide followed by cooling in an atmosphere of carbon dioxide containing methyl alcohol vapour gives accurate results, whereas the method of heating in hydrogen alone is stated to lead to erroneous results.[40]

An iodometric determination of lead depending upon the precipitation of lead as sulphite has been worked out.[41] Knop's titration of dichromate and iron in the presence of diphenylamine as indicator is applied to the determination of lead obtained as chromate.[42] Some caution is necessary with dilute solutions or lead nitrate used as standards. These appear to undergo hydrolysis on keeping, the lead content segregating towards the bottom of top layers according as the water used is boiled or not, and interaction of the lead salt with the glass is also involved.[43]

Bismuth may be separated from lead by means of pyrogallol, with which bismuth forms a precipitate quantitatively.[44] Freshly prepared bismuth sulphide is completely soluble at 30° in hydrochloric acid—1 of concentrated acid to 3 of water—whilst precipitation as sulphide is complete in 1 : 5 acid.[45] The deep red colour given by bismuth iodide with bases, *e.g.*, tetra-acetylammonium hydroxide, may be utilised for the determination of small amounts of bismuth in tissue, etc.[46]

For the separation of cadmium from zinc by means of hydrogen sulphide in acid solution, definite minimum acidity is necessary. Ammonium sulphate assists the precipitation;[47] the cadmium may

[37] H. T. S. Britton, *J.*, 1925, **127**, 2110—2159.
[38] G. Spacu, *Z. anal. Chem.*, 1925, **67**, 27; *A.*, ii, 1004.
[39] A. Jilek and J. Lukas, *Chem. Listy*, 1925, **19**, 275; *A.*, ii, 903.
[40] F. L. Hahn, *Z. anal. Chem.*, 1924, **65**, 134; *A.*, 1925, ii, 160.
[41] C. E. Richards, *Analyst*, 1925, **50**, 398; *A.*, ii, 903.
[42] W. W. Scott, *Ind. Eng. Chem.*, 1925, **17**, 678; *A.*, ii, 903.
[43] H. Bernhardt, *Z. anal. Chem.*, 1925, **67**, 97; *A.*, ii, 1003.
[44] F. Feigl and H. Ordelt, *ibid.*, 1925, **65**, 448; *A.*, ii, 442.
[45] S. Ramachandran, *Chem. News*, 1925, **131**, 135; *A.*, ii, 1005.
[46] A. Girard and E. Fourneau, *Compt. rend.*, 1925, **181**, 610; *A.*, ii, 1207.
[47] G. Luff, *Z. anal. Chem.*, 1924, **65**, 97; *A.*, 1925, ii, 159.

subsequently be precipitated and weighed as cadmium diammonium ferrocyanide.[48]

Improvements in the separation of arsenic from antimony and tin by distillation of the chlorides have been effected, and it is found that the volatilisation of the arsenic chloride is complete if a current of carbon dioxide is passed through the apparatus maintained at water-bath temperature for 2 hours.[49] A more rapid quantitative separation of the arsenic is stated to be obtained if the special flask described provided with a fractionating inset is employed.[50]

Iron may be precipitated as hydroxide from hot dilute solutions containing an excess of ammonium thiocyanate by means of pyridine, thereby allowing a separation from mercury.[51] The high results obtained by ignition of ferric hydroxide precipitated by ammonia may be rectified by a second ignition following on treatment with a little nitric acid.[52] Conditions have been worked out, especially with reference to ores, for the complete separation of nickel and copper from iron by means of ammonia and ammonium salts.[53]

For the colorimetric determination of iron, the ferrocyanide method is preferred to the thiocyanate method, with which phosphates interfere.[54] The difficulty in determining iron by salicylic acid or as thiocyanate when tartaric and citric acids are present is surmounted by taking advantage of the blue colour produced by alloxantin with ferric iron in alkaline solutions.[55]

Aluminium, like iron and manganese, is precipitated on boiling solutions of its salts with hexamethylenetetramine, which possesses the advantage over ammonia that it does not absorb carbon dioxide and so avoids contamination of the precipitate with calcium.[56] Aluminium hydroxide, again like iron, precipitated by means of "infusible white precipitate" ($ClHg{\cdot}NH_2$) filters more readily than the form produced by ammonia and is separated completely from manganese in one operation.[57] Either sodium alizarinsulphonate or the colouring matter of pæonies may be used as indicator with

[48] G. Luff, *Chem. Ztg.*, 1925, **49**, 513; *A.*, ii, 826.
[49] K. Röhre, *Z. anal. Chem.*, 1924, **65**, 109; *A.*, 1925, ii, 157.
[50] F. L. Hahn and H. Wolf, *Ber.*, 1924, **57**, [*B*], 1858; *A.*, 1925, ii, 68.
[51] G. Spacu, *Z. anal. Chem.*, 1925, **67**, 147; *A.*, ii, 1206.
[52] N. A. Tananaev, *Z. anorg. Chem.*, 1924, **136**, 184; *A.*, 1925, ii, 603.
[53] E. G. R. Ardagh and G. M. Broughall, *Univ. Toronto, Sch. Eng. Res. Bull.*, 1925, **5**, 227; *A.*, ii, 603.
[54] W. B. Walker, *Analyst*, 1925, **50**, 279; *A.*, ii, 717.
[55] G. Denigès, *Compt. rend.*, 1925, **180**, 519; *A.*, i, 441.
[56] C. Kollo and N. Georgian, *Bul. Soc. Chim. România*, 1924, **6**, 111; *A.*, 1925, ii, 330.
[57] B. Solaja, *Chem. Ztg.*, 1925, **49**, 337; *A.*, ii, 602.

potassium hydroxide for determining excess of sulphuric acid in a solution of aluminium sulphate.[58] In another method, the aluminium salt is converted into a complex oxalato-compound by treatment with excess of alkali oxalate, and the "residual" acidity determined iodometrically.[59]

Boiling with sodium nitrite has been applied as a means of separating iron, chromium, aluminium, and phosphoric acid from zinc, nickel, cobalt, and manganese.[60] Sulphosalicylic acid also has been used for various separations in this group.[61]

For the determination of zinc in solutions containing alkali or magnesium salts, precipitation with thiocyanate and pyridine followed by ignition to oxide gives satisfactory results;[62] cyanamide also can be used for this purpose.[63]

Two volumetric methods of determining manganese have been described, one using permonophosphoric acid,[64] the other depending on the precipitation of manganous chromate[65] ($MnCrO_4,2H_2O$) by means of potassium chromate and titration of the excess of chromate.

In the dimethylglyoxime determination of nickel in the presence of iron and cobalt, high results are obtained due to the precipitation of an iron–cobalt–glyoxime unless the iron be in the ferrous condition.[66] α-Furildioxime[67] and oxalenediuramidoxime[68] also are reagents for nickel. Details are given for a colorimetric determination of cobalt in presence of nickel, utilising the colour produced by ammonia and sodium peroxide.[69]

It is found that citric acid does not prevent the complete precipitation of calcium provided sufficient excess of ammonium oxalate is used,[70] and it has the advantage of causing the calcium oxalate to separate in a form not isomorphous with magnesium

[58] T. Sabalitschka and G. Reichel, *Arch. Pharm.*, 1925, **263**, 193; *A.*, ii, 602.

[59] F. Feigl and G. Krauss, *Ber.*, 1925, **58**, [*B*], 398; *A.*, ii, 329.

[60] K. K. Järvinen, *Z. anal. Chem.*, 1925, **66**, 81; *A.*, ii, 602.

[61] L. Moser and A. Brukl, *Ber.*, 1925, **58**, [*B*], 380; *A.*, ii, 329.

[62] L. A. Congdon, A. B. Guss, and F. A. Winter, *Chem. News*, 1925, **131**, 65, 81, 97, 113; *A.*, ii, 1002.

[63] W. Marckwald and H. Gebhardt, *Z. anorg. Chem.*, 1925, **147**, 42; *A.*, ii, 1002.

[64] T. Heczko, *ibid.*, 1925, **143**, 129; *A.*, ii, 440.

[65] B. N. Angelescu, *Bul. Soc. Chim. România*, 1924, **6**, 109; *A.*, 1925, ii, 330.

[66] J. G. Weeldenburg, *Rev. trav. chim.*, 1924, **43**, 465; *A.*, 1925, ii, 72.

[67] B. A. Soule, *J. Amer. Chem. Soc.*, 1925, **47**, 981; *A.*, ii, 603.

[68] F. Feigl and A. Christiani-Kronwald, *Z. anal. Chem.*, 1925, **65**, 341; *A.*, ii, 330.

[69] B. S. Evans, *Analyst*, 1925, **50**, 389; *A.*, ii, 904.

[70] W. F. Jakób, *Roczniki Chemii*, 1923, **3**, 308; *A.*, 1925, ii, 69.

oxalate.[71] The question of the accuracy of the oxalate separation of calcium and magnesium has been examined again during the year by several observers and suggestions for the best conditions of separation are given.[72]

Sodium salts are preferable to ammonium salts as precipitants for magnesium ammonium phosphate or arsenate.[73] The accurate determination of magnesium in aluminium alloys is nowadays of considerable importance. Small amounts of magnesium in the presence of large quantities of aluminium are conveniently separated from most of the latter by precipitation with excess of alkali hydroxide,[74] since the direct deposition of magnesium ammonium phosphate in the presence of tartaric acid requires several days.[75]

Mixed solvents consisting of alcohols and ethyl acetate are advocated for the separation of the alkali perchlorates.[76] The determination of alkalis by Berzelius's process in silicate analysis may be hastened by heating to dull redness the product of the hydrofluoric–sulphuric acid treatment; extraction of the cold mass with water leaves a residue free from alkalis.[77] A practicable scheme for determining silica and lithium in lithium minerals is described.[78]

Small proportions of iron and aluminium may be removed from gallium by precipitation with excess of ammonium hydroxide,[79] whilst gallium may be separated from many metals with which it occurs by extraction of its solution in 5—6*N*-hydrochloric acid with ether.[80]

For the oxidation of precipitated germanium disulphide, hydrogen peroxide acting on an ammoniacal solution of the sulphide is preferred to the more customary nitric acid.[81]

Iron may be separated from tantalum and columbium as sulphide by adding oxalic and tartaric acids and then rendering alkaline

[71] W. F. Jakób, *Roczniki Chemji*, 1925, **5**, 159; *A.*, ii, 1095.

[72] Bach, *Chem. Ztg.*, 1925, **49**, 514; *A.*, ii, 825; R. Heilingötter, *ibid.*, 241; *A.*, ii, 437; V. Rodt and E. Kindscher, *ibid.*, 1924, **48**, 953, 964; *A.*, 1925, ii, 158; G. Luff, *Z. anal. Chem.*, 1925, **65**, 439; *A.*, ii, 438.

[73] L. A. Congdon and G. Vanderhook, *Chem. News*, 1925, **130**, 241, 258, 273; *A.*, ii, 601.

[74] F. L. Hahn and S. Scheiderer, *Ber.*, 1924, **57**, [*B*], 1854; *A.*, 1925, ii, 69.

[75] G. Jander, E. Wendehorst, and B. Weber, *Z. anorg. Chem.*, 1925, **142**, 329; *A.*, ii, 715.

[76] G. F. Smith and J. F. Ross, *J. Amer. Chem. Soc.*, 1925, **47**, 762, 774, 1020; *A.*, ii, 436, 437, 601.

[77] O. Cantoni, *Z. anal. Chem.*, 1925, **67**, 33; *A.*, ii, 1001.

[78] A. Guntz and F. Benoit, *Bull. Soc. chim.*, 1925, [iv], **37**, 1294; *A.*, ii, 1202.

[79] R. Fricke, *Z. anorg. Chem.*, 1925, **144**, 267; *A.*, ii, 717.

[80] E. H. Swift, *J. Amer. Chem. Soc.*, 1924, **46**, 2375; *A.*, 1925, ii, 71.

[81] E. B. Johnson and L. M. Dennis, *ibid.*, 1925, **47**, 790; *A.*, ii, 442.

with ammonia. The rare metals are separated from the treated filtrate from the iron sulphide by means of "cupferron." [82] The two metals can be separated from each other [83] by a process depending on the differential hydrolytic dissociation between oxalotantalic and oxalocolumbic acids in the presence of tannin.

Sexavalent uranium salts are preferably reduced to the quadrivalent form by means of lead and hydrochloric acid prior to titration, since the usual metallic reducing agents always produce slight over-reduction.[84] Rare earths may be satisfactorily separated from uranium by the oxalate method by conversion of the uranium into uranylsalicylic acid.[85]

The vanadium in a vanadate solution, obtained by oxidation with alkaline hydrogen peroxide solution, may be determined iodometrically,[86] whilst vanadium may be determined in the presence of iron, *e.g.*, in a vanadium steel, by titration with ferrous iron with diphenylamine as indicator.[87]

From nitrite solution, small amounts of palladium can be cleanly precipitated by means of dimethylglyoxime in the presence of large quantities of platinum; [88] when, however, the proportion of palladium is high, precipitation with α-nitroso-β-naphthol, acetylene, dimethylglyoxime, or mercuric cyanide yields a bulky precipitate which retains some platinum. In such a case, prior removal of the latter metal as ammonium chloroplatinate is recommended.[89] Platinum may be quantitatively separated from ruthenium by treatment with sodium hydroxide, glycerol, and bromine.[90]

Conditions have been worked out for the separation of zirconium and hafnium from titanium, cerium, and thorium by means of sodium arsenate.[91]

Molybdenum trisulphide may be obtained in a form which filters readily by acidification of the molybdate solution treated with fresh ammonium polysulphide. It affords an oxide, on gentle roasting, which may contain traces of ferric oxide, silica, zinc oxide, copper oxide and vanadium pentoxide; these should be determined and correction made for them.[92] In the conversion of

[82] H. Pied, *Compt. rend.*, 1924, **179**, 897; *A.*, 1925, ii, 442.
[83] A. R. Powell and W. R. Schoeller, *Analyst*, 1925, **50**, 485; *A.*, ii, 1096.
[84] O. Koblic, *Chem. Listy*, 1925, **19**, 1; *A.*, ii, 331.
[85] G. Canneri and L. Fernandes, *Gazzetta*, 1924, **54**, 770; *A.*, 1925, ii, 71.
[86] A. E. Stoppel, C. F. Sidener, and P. H. M-P. Brinton, *J. Amer. Chem. Soc.*, 1924, **46**, 2448; *A.*, 1925, ii, 73.
[87] K. Someya, *Z. anorg. Chem.*, 1924, **139**, 237; *A.*, 1925, ii, 161; N. H. Furman, *Ind. Eng. Chem.*, 1925, **17**, 314; *A.*, ii, 442.
[88] H. E. Zschiegner, *Ind. Eng. Chem.*, 1925, **17**, 294; *A.*, ii, 443.
[89] F. Krauss and H. Deneke, *Z. anal. Chem.*, 1925, **67**, 86; *A.*, ii, 1005.
[90] O. Ruff and E. Vidic, *Z. anorg. Chem.*, 1925, **143**, 163; *A.*, ii, 443.
[91] L. Moser and R. Lessing, *Monatsh.*, 1924, **45**, 323; *A.*, 1925, ii, 718.
[92] W. Hartmann, *Z. anal. Chem.*, 1925, **67**, 152; *A.*, ii. 1206.

molybdenum sulphide into oxide by ignition, a temperature of 600° should not be exceeded.[93] Two colorimetric methods of determining molybdenum in the form of sulphide [94] or thiomolybdate [95] in acid and ammoniacal solutions, respectively, are described.

In the determination of boric acid through the methyl ester, aluminium, chromium, and iron must first be removed. A procedure for securing the removal of these metals without loss of boric acid is described.[96] This acid may be titrated with sodium hydroxide in the presence of saturated solutions of salts, *e.g.*, calcium or lithium chloride, which are strong dehydrating agents.[97] The suggestion is made that the boric acid titration becomes possible through dehydration. This may be so with glycerol, but scarcely seems probable with mannitol, invert-sugar, and other compounds, seeing how small a concentration of these last is required.

Mohr's chloride–silver titration can be carried out in faintly acid solution (p_H 5 to 7) by addition of a sodium acetate-acetic acid buffer mixture to reduce the acidity.[98] By treating a solution containing cyanides and halogen salts with sodium hydrogen carbonate and formaldehyde, the cyanides are eliminated as glycollates and hexamethylenetetramine, thus allowing the application of Volhard's method for halogens or thiocyanates in the usual way.[99] Reduction of chlorates in the presence of ferrous sulphate is most nearly complete (99%) in acid solution in the presence of potassium iodide.[1] A critical study of several different methods for the evaluation of chlorates has been made, with the result that all the methods, except one, were found satisfactory.[2]

The accurate determination of small amounts of fluorine is a well-known analytical difficulty. Precipitation by calcium or thorium salts is unsatisfactory, for which purpose lanthanum acetate is now proposed.[3] The process would, however, seem to present certain difficulties, since a correction must be made for adsorbed precipitant.

In the determination of large amounts of phosphoric acid by the molybdate-magnesia method, high or low results are obtained according as the solution of the yellow precipitate in aqueous

[93] P. H. M-P. Brinton and A. E. Stoppel, *J. Amer. Chem. Soc.*, 1924, **46**, 2454; *A.*, 1925, ii, 72.
[94] E. Wendehorst, *Z. anorg. Chem.*, 1925, **144**, 319; *A.*, ii, 718.
[95] H. ter Meulen, *Chem. Weekblad*, 1925, **22**, 80; *A.*, ii, 330.
[96] H. Funk and H. Winter, *Z. anorg. Chem.*, 1925, **142**, 257; *A.*, ii, 714.
[97] M. Cikrtová and K. Šandera, *Chem. Listy*, 1925, **19**, 179; *A.*, ii, 714.
[98] H. W. Doughty, *J. Amer. Chem. Soc.*, 1924, **46**, 2707; *A.*, 1925, ii, 238.
[99] E. Schulek, *Z. anal. Chem.*, 1925, **65**, 433; *A.*, ii, 432.
[1] C. O. Harvey, *Analyst*, 1925, **50**, 538; *A.*, ii, 1197.
[2] E. C. Wagner, *Ind. Eng. Chem.*, 1925, **17**, 1183; *A.*, ii, 1196.
[3] R. J. Meyer and W. Schulz, *Z. angew. Chem.*, 1925, **38**, 203; *A.*, ii, 598.

ammonia is acid or alkaline to litmus [4] or more conveniently to bromothymol-blue,[5] correct values being given at the neutral point. Other chemists,[6] however, find that the precipitate from neutral solution is contaminated with magnesium molybdate and the normal phosphate. As these writers obtain satisfactory precipitation from slightly acid solution, it would seem that there is some further condition for precipitation not yet definitely laid down. The Pemberton-Neumann method has been studied for the purpose of eliminating errors,[7] and an improved method of producing a precipitate of magnesium ammonium phosphate free from other magnesium phosphates is described.[8] Phosphates may be rapidly determined by precipitation with silver nitrate in presence of a slight excess of sodium acetate, the silver content of the precipitate after dissolving in nitric acid being determined by titration with thiocyanate.[9]

Selenium may be quantitatively separated from tellurium by precipitation by sulphur dioxide from cold solution of the two oxides in concentrated hydrochloric acid.[10] Hydroxylamine hydrochloride is found to be superior to hydrazine salts for the same separation, the oxides being dissolved in hydrochloric, tartaric, or citric acid.[11]

A rapid method of evaluating elementary sulphur is the oxidation with hydrogen peroxide of the solution of sulphur in a known volume of hot standard sodium hydroxide.[12] Sulphites may be determined accurately by titration with iodate, free bromine, bromate, permanganate, or dichromate solutions containing iodide.[13] In the absence of iodides, the amounts of bromate and dichromate used are less than those required for complete conversion of sulphite into sulphate, due, it is suggested, to the formation of dithionic acid. Iodate alone oxidises sulphites to sulphates completely.[14] Methods

[4] J. M. McCandless and J. Q. Burton, *Ind. Eng. Chem.*, 1924, **16**, 1267; *A.*, 1925, ii, 157.

[5] W. H. Ross, R. M. Jones, and A. R. Merz, *J. Assoc. Off. Agric. Chem.*, 1925, **8**, 407.

[6] G. Jørgensen, *Z. anal. Chem.*, 1925, **66**, 209; *A.*, ii, 824; R. J. Caro and E. L. Larison, *Ind. Eng. Chem.*, 1925, **17**, 261.

[7] M. B. Richards and W. Godden, *Analyst*, 1924, **49**, 565; *A.*, 1925, ii, 66; compare P. Nyssens, *Bull. Soc. chim. Belg.*, 1925, **34**, 232; *A.*, ii, 1201.

[8] B. Schmitz, *Z. anal. Chem.*, 1924, **65**, 46; *A.*, 1925, ii, 67.

[9] R. F. Le Guyon and R. M. May, *Bull. Soc. chim.*, 1925, [iv], **37**, 1291; *A.*, ii, 1202.

[10] V. Lenher and C. H. Kao, *J. Amer. Chem. Soc.*, 1925, **47**, 769; *A.*, ii, 434.

[11] *Idem, ibid.*, 2454; *A.*, ii, 1199.

[12] F. Kühl, *Z. anal. Chem.*, 1924, **65**, 185; *A.*, 1925, ii, 156.

[13] W. S. Hendrixson, *J. Amer. Chem. Soc.*, 1925, **47**, 2156; *A.*, ii, 1001.

[14] *Idem, ibid.*, 1319; *A.*, ii, 712.

are described for the volumetric determination of various sulphur acids in admixture.[15]

Some notes on Nessler's solution have been published,[16] and a modified reagent is described avoiding the use of potassium iodide.[17]

Of various phenols tested, resorcinol and phloroglucinol alone can replace phenol as fixing agents for nitrate nitrogen by the Kjeldahl process in the absence of an accelerator. Even when phenol itself is used, the potassium sulphate should not be added until the first main reaction is completed.[18]

Water Analysis.

For the detection of silicic acid in distilled water or sodium chloride, potassium molybdate in nitric acid is added to the warm liquid. The green colour of the potassium silicomolybdate solution may be compared with that obtained from a standard sodium silicate solution.[19] In many investigations, the presence of traces of copper in water is undesirable. This metal may be detected in distilled water by adding a few drops of dilute hydrogen peroxide solution followed by alcohol. A characteristic blue coloration is produced, if copper is present, when a solution of alcohol-soluble guaiacum resin in pyridine is added to the water–alcohol mixture. The coloured substance is soluble in chloroform and ethyl acetate, the limit of sensitiveness is 1 in 10^8.[20] Lead may be isolated from water for the purpose of colorimetric determination by precipitating the liquid with ammonia after addition of aluminium sulphate and sulphuric acid.[21] An improved method of preparing the *o*-tolidine solution for the determination of chlorine in chlorinated water is described.[22]

In comparing the dissolved carbon dioxide content of different liquids, it has been found of value to determine the quantity of alkali necessary to lower the hydrogen-ion concentration to a fixed level. The method of comparison chosen is that of determining the amount of carbon dioxide carried over when air is passed through the

[15] A. Kurtenacker and K. Bittner, *Z. anorg. Chem.*, 1924, **141**, 297; 1925, **142**, 115, 119; *A.*, ii, 239, 433, 434; E. Schulek, *Z. anal. Chem.*, 1925, **65**, 352.

[16] H. D. Richmond, *Analyst*, 1925, **50**, 67; *A.*, ii, 327; R. C. Frederick, *ibid.*, 183; *A.*, ii, 435.

[17] L. W. Winkler, *Z. Unters. Nahr. Genussm.*, 1925, **49**, 163; *A.*, ii, 713.

[18] B. M. Margosches and E. Scheinost, *Ber.*, 1925, **58**, [*B*], 1850, 1857; *A.*, ii, 1094.

[19] R. Lorenz and E. Bergheimer, *Z. anorg. Chem.*, 1924, **136**, 95; *A.*, 1925, ii, 600.

[20] G. Poirot, *J. Pharm. Chim.*, 1924, [vii], **30**, 393; *A.*, 1925, ii, 242.

[21] W. W. Scott, *Chem. News*, 1925, **131**, 17; *A.*, ii, 903.

[22] C. E. Roake, *Ind. Eng. Chem.*, 1925, **17**, 257; *A.*, ii, 432.

different samples of water maintained at a definite hydrogen-ion concentration.[23] A form of flask has been described with the view of preventing the introduction of air when the reagents are introduced into the water in Winkler's method for determining dissolved oxygen.[24] Nitrous acid, which interferes seriously with this determination, may be removed by sodium azide.[25]

A comparison of the Sörensen values of samples of sea-water of known salinity as determined by electrometric and colorimetric methods using cresol-red has supplied the correction for the "salt error" of this indicator. Tables are given for the corrections to be applied to the colorimetric determinations.[26]

In solutions containing only small quantities of electrolytes, some indicators show a too acid reaction; for such solutions the indicators advised are α-naphthol-blue, cresol-red, neutral red, bromothymol-blue, bromocresol-purple, methyl-red, and methyl-orange.[27]

Gas Analysis.

Several modifications of apparatus have been recorded from among which may be noted an improved form of the Bone and Wheeler type with which samples of from 1 to 5 ml. of gas may be accurately analysed;[28] one in which the absorption vessel can be readily detached from the burette and placed in a shaking machine so that four or five sets of absorption vessels may be used in rotation;[29] and another for the accurate determination of small quantities of hydrogen, methane, etc., in the presence of a large excess of oxygen (or *vice versa*) in which the gases, after passing through a combustion chamber, enter a hair hygrometer, the alterations in the length of the fibre being an indication of the water content, *i.e.*, of the hydrogen or oxygen content of the original gas.[30]

Attention is directed to the fact that oxidation of absorbed oxides of nitrogen by hydrogen peroxide in sodium hydroxide solution—assumed in several recent researches to be complete—leads to formation of nitrite. For complete oxidation, the gases are shaken in a closed bottle with acidified hydrogen peroxide for

[23] R. Legendre, *Compt. rend.*, 1925, **180**, 1527; *A.*, ii, 714.
[24] J. N. Friend, *Chem. News*, 1925, **130**, 163; *A.*, ii, 326.
[25] G. Alsterberg, *Biochem. Z.*, 1925, **159**, 36; *A.*, ii, 1198.
[26] W. D. Ramage and R. C. Miller, *J. Amer. Chem. Soc.*, 1925, **47**, 1230; *A.*, ii, 712.
[27] I. M. Kolthoff, *Rec. trav. chim.*, 1925, **44**, 275; *A.*, ii, 596.
[28] D. S. Chamberlin and D. M. Newitt, *Ind. Eng. Chem.*, 1925, **17**, 621; *A.*, ii, 710.
[29] M. N. J. Dirken, *J. Scientific Instruments*, 1924, **2**, 55; *A.*, 1925, ii, 154.
[30] L. Löwenstein, *Z. physikal. Chem.*, 1924, **110**, 799; *A.*, 1925, ii, 154.

3 hours; very small amounts such as occur normally in the air or in products of combustion are separated by passing a measured volume of the gas through tubes cooled in liquid air, the condensate being then oxidised as above for the purpose of determination.[31]

Hydrogen and carbon monoxide are completely burnt to water and carbon dioxide, respectively, whilst methane remains unchanged, when brought into contact with copper oxide at 280—290°. Mixtures of these gases may thus be analysed, preferably in a special gas pipette, which may be exhausted before introduction of the gases, so that errors due to absorption of air by the contact mass of ceric and copper oxides may be eliminated.[32]

The amount of carbon dioxide in a gaseous mixture may be determined by measuring the volume condensed by means of liquid air; carbon monoxide is determined by oxidation, after removal of condensible gases, over heated iodine pentoxide, followed by liquefaction.[33] Except in the case of fresh ammoniacal solution containing not more than 5% of its volume of dissolved carbon monoxide, cuprous chloride does not absorb this gas to completeness;[34] the slower absorption by cuprous oxide in sulphuric acid containing β-naphthol may be hastened by using the reagent at a temperature of about 60°.[35]

A sensitive qualitative method for the detection of oxygen has been devised dependent upon a coloration with pyrogallol and potassium hydroxide; nitrogen, hydrogen, acetylene, carbon monoxide, nitrous acid, nitric oxide, and ammonia do not interfere.[36] For another test, the oxygen is allowed to react with purified nitric oxide, the higher oxides of nitrogen affording a coloration with a sulphuric acid solution of diphenylamine or with a dilute acetic acid solution of α-naphthylamine and sulphanilic acid.[37] The completeness and rapidity of absorption of oxygen by alkaline sodium hyposulphite are increased by the addition of 2% of sodium anthraquinone-2-sulphonate.[38]

Dilute ozonised air may be analysed with moderate accuracy by rapidly bubbling a large volume through potassium iodide, the

[31] A. G. Francis and A. T. Parsons, *Analyst*, 1925, **50**, 262; *A.*, ii, 713.

[32] J. Švéda, *Chem. News*, 1925, **130**, 1; *Chem. Listy*, 1925, **19**, 41; *A.*, ii, 154, 432.

[33] P. Lebeau and P. Marmasse, *Compt. rend.*, 1925, **180**, 1847; *A.*, ii, 824.

[34] H. R. Ambler, *Analyst*, 1925, **50**, 167; *A.*, ii, 436.

[35] T. C. Sutton and H. R. Ambler, *ibid.*, 172; *A.*, ii, 436.

[36] H. Schmalfuss and H. Werner, *Ber.*, 1925, **58**, [*B*], 71; *A.*, ii, 238.

[37] *Idem*, *J. pr. Chem.*, 1925, [ii], **111**, 62; *A.*, ii, 1198.

[38] L. F. Fieser, *J. Amer. Chem. Soc.*, 1924, **46**, 2639; *A.*, 1925, ii, 238.

iodine liberated being titrated with arsenite solution. Colorimetric comparison with standards is stated to be unsatisfactory.[39]

Organic Analysis.

Qualitative.—In cases of poisoning by formaldehyde, tests may be applied directly to pieces of stomach wall;[40] an intense magenta-red coloration with Schryver's reagent is not, as hitherto supposed, specific for formaldehyde, since it is given by very small amounts of glyoxylic acid. The presence of formaldehyde in green leaves cannot be considered as proved.[41] Glycerol gives a positive coloration in 0·04% solution by treatment with Schiff's reagent, following oxidation with permanganate.[42]

Citric acid may be detected by oxidation with potassium dichromate to acetone, which is identified by appropriate methods;[43] and in the presence of tartaric acid by the blue coloration given with an acid solution of phosphomolybdic and vanadic acids.[44] Lactic acid may be detected, *e.g.*, in fruit juices containing other organic acids, by reason of the solubility of calcium lactate and the insolubility of the other calcium salts in 75% alcohol.[45]

The test for acetone with sodium nitroprusside in ammoniacal solution is most sensitive in the presence of ammonium sulphate;[46] full details of the colorations given by acetone and by acetaldehyde with nitroprusside in alkaline and acid solutions are tabulated.[47]

Methylamine may be detected in the presence of large amounts of ammonia by the formation of dinitromethylaniline from chloro-2 : 4-dinitrobenzene.[48] A number of *m*-nitrobenzenesulphonamides have been described as being particularly useful for the identification of secondary amines.[49] The colour reaction following oxidation with chromic acid serves to identify aniline and the three toluidines.[50] Ammonia even in small amounts should be removed by aëration before application of the hypochlorite reaction for aniline.[51]

[39] H. von Wartenberg and G. von Podjaski, *Z. anorg. Chem.*, 1925, **148**, 391; *A.*, ii, 1198.
[40] C. Ghigliotto, *Ann. Chim. Analyt.*, 1925, [ii], **7**, 39; *A.*, ii, 445.
[41] R. Fosse and A. Hieulle, *Compt. rend.*, 1924, **179**, 636; *A.*, 1925, ii, 162.
[42] I. M. Kolthoff, *Pharm. Weekblad*, 1924, **61**, 1497; *A.*, 1925, ii, 161.
[43] Rodillon, *Repert. Pharm.*, 1924, **35**, 233; *A.*, 1925, ii, 246.
[44] W. Parri, *Giorn. Chim. Ind. Appl.*, 1924, **6**, 537; *A.*, 1925, ii, 162.
[45] A. Bornträger, *Z. anal. Chem.*, 1925, **66**, 430; *A.*, ii, 1007.
[46] H. W. van Urk, *Pharm. Weekblad*, 1925, **62**, 8; *A.*, ii, 162.
[47] *Idem, ibid.*, 2; *A.*, ii, 162.
[48] P. A. Valton, *J.*, 1925, **127**, 40.
[49] C. S. Marvel, F. L. Kingsbury, and F. E. Smith, *J. Amer. Chem. Soc.*, 1925, **47**, 166; *A.*, i, 244.
[50] H. D. Murray, *Chem. News*, 1925, **130**, 23; *A.*, ii, 163.
[51] E. S. West, *Ind. Eng. Chem.*, 1924, **16**, 1270; *A.*, 1925, ii, 163.

Tertiary amyl alcohol in sulphuric acid affords a colour reaction with tartaric acid and guaiacol,[52] whilst benzyl alcohol may be detected when present in fair proportion with hydrocarbons, alcohols, ketones, etc., by conversion into benzyl oxalate.[53]

A qualitative test for weak organic bases depends upon the formation of ferrichlorides upon interaction of the base and ferric chloride.[54]

Various reactions are given for distinguishing the different alkyl derivatives of barbituric acid used as hypnotics.[55]

Colour changes are described for thirteen opium alkaloids when treated in glacial acetic acid solution with basic magnesium hypochlorite and poured upon the surface of concentrated sulphuric acid.[56] The melting points, solubilities, and microscopic appearance of the picrates of several opium alkaloids are described.[57]

A blue coloration, characteristic of pentoses, develops when an aqueous solution of a pentose or of derivatives containing pentose is poured upon a solution of β-naphthol in concentrated sulphuric acid.[58] Pure glycyrrhizin, owing to its glucosidic nature, gives an immediate violet coloration in presence of sulphuric acid and aromatic hydroxyaldehydes.[59]

Pyrocatechol tannins give a heavy precipitate with nitrosomethylurethane, most pyrogallol tannins giving no precipitate. When treated twice with this reagent and then with iron alum and sodium acetate, pyrogallol tannins develop a typical blue coloration, not given by pyrocatechol tannins.[60] Two useful modifications of the ferric citrate precipitation test for tannins have been described,[61] and also some notes on the identification of drugs containing tannins.[62]

A greenish-blue colour test for Grignard reagent is obtained on treatment with Michler's ketone, water, and iodine.[63]

A comparative study has been made of the sensitiveness of the various tests for small amounts of α-naphthol in β-naphthol;[64]

[52] L. Ekkert, *Pharm. Zentr.*, 1925, **66**, 599; *A.*, ii, 1006.
[53] A. S. Pfau, *Perf. Ess. Oil Rec.*, 1925, **16**, 190; *A.*, ii, 905.
[54] R. Robinson, *J.*, 1925, **127**, 768.
[55] A. Zamparo, *Boll. Chim. Farm.*, 1925, **64**, 257; *A.*, ii, 907.
[56] L. David, *Pharm. Ztg.*, 1925, **70**, 969; *A.*, ii, 1010.
[57] C. W. Maplethorpe and N. Evers, *Pharm. J.*, 1925, **115**, 137; *A.*, i, 1166.
[58] P. Thomas, *Bull. Soc. Chim. biol.*, 1925, **7**, 102; *A.*, ii, 604.
[59] P. Bertolo, *Giorn. Chim. Ind. Appl.*, 1925, **7**, 404; *A.*, ii, 1212.
[60] W. Vogel, *Collegium*, 1925, 189; *A.*, ii, 827.
[61] A. H. Ware, *Analyst*, 1925, **50**, 335; *A.*, ii, 905.
[62] *Idem*, *Pharm. J.*, 1925, **115**, 131; *A.*, ii, 1209.
[63] H. Gilman and F. Schulze, *J. Amer. Chem. Soc.*, 1925, **47**, 2002; *A.*, ii, 1011.
[64] T. Callan, *J. Soc. Chem. Ind.*, 1925, **44**, 125T; *A.*, ii, 444.

these two substances may be differentiated by means of their colour reactions with sulphuric acid in alcoholic solution containing hydrogen peroxide and with formaldehyde in the presence of hydrochloric acid.[65] Benzyl-ψ-thiocarbamide forms salts with various naphthalenesulphonic acids, usually of definite melting point and suitable for use as a means of identifying the acids.[66]

Quantitative.—Numerous papers have appeared dealing with the ultimate analysis of organic compounds, of which perhaps the most interesting describes in detail a volumetric method for carbon and hydrogen in which the products of combustion other than carbon dioxide and water vapour are removed by appropriate means. Reaction of the water with heated " naphthyloxychlorophosphine," $C_{10}H_7 \cdot POCl_2$, liberates hydrogen chloride equivalent to the hydrogen in the substance; the gases are washed with a small volume of water to retain the hydrogen chloride, and the carbon dioxide is absorbed in excess of standard barium hydroxide. Titration of the hydrochloric acid gives the hydrogen content of the substance, and titration of the excess of barium hydroxide gives the carbon content. Details of the apparatus and preparation of the reagents are given.[67] Descriptions of the chromic acid oxidation [68] and of a rapid calorimetric bomb method are furnished.[69] Following oxidation of an organic compound with potassium iodate and sulphuric acid (the carbon dioxide evolved being determined in the usual way), a determination of the excess of iodate affords data for calculating the composition.[70] Modifications of well-known methods for carbon, hydrogen, and nitrogen consist in the use of manganese dioxide at 400° and upwards [71] and in combustion with copper oxide in a vacuum.[72]

If the decomposition of hydrazine in alcoholic potash solution into nitrogen and hydrogen by a catalyst prepared from palladium chloride be carried out in the presence of an organic halogen compound, the halogen is eliminated and can be determined.[73] Sodium arsenite in alkaline solution may be used as a reagent for loosely combined halogen.[74]

[65] A. Zamparo, *Boll. Chim. Farm.*, 1925, **64**, 97; *A.*, ii, 444.

[66] R. F. Chambers and P. C. Scherer, *J. Ind. Eng. Chem.*, 1924, **16**, 1272; *A.*, 1925, i, 127.

[67] J. Lindner, *Z. anal. Chem.*, 1925, **66**, 305; *A.*, ii, 901.

[68] J. W. White and F. J. Holben, *Ind. Eng. Chem.*, 1925, **17**, 83; *A.*, ii, 240; A. Desgrez and R. Vivario, *Compt. rend.*, 1925, **180**, 886; *A.*, ii, 436.

[69] H. D. Wilde, jun., and H. L. Lochte, *J. Amer. Chem. Soc.*, 1925, **47**, 440; *A.*, ii, 600.

[70] G. Vortmann, *Z. anal. Chem.*, 1925, **66**, 272; *A.*, ii, 827.

[71] J. Heslinga, *Rec. trav. chim.*, 1924, **43**, 551; *A.*, 1925, ii, 65.

[72] J. Švéda and O. Pročke, *Chem. Listy*, 1925, **19**, 163; *A.*, ii, 719.

[73] M. Busch, *Z. angew. Chem.*, 1925, **38**, 519; *A.*, ii, 823.

[74] A. Gutmann, *Z. anal. Chem.*, 1924, **65**, 246; *A.*, 1925, ii, 238.

The nitrogen in oil, coke, and proteins is converted quantitatively into ammonia by admixture with sodium carbonate and heating in a current of moist hydrogen at 100°; [75] catalytic hydrogenation is similarly applied to organic nitrogen compounds.[76]

Destruction of organic matter with 30% hydrogen peroxide prior to the determination of inorganic poisons in viscera, etc., is described; [77] whilst a rapid method for the determination of arsenic in organic compounds depends upon decomposition with ammonium persulphate.[78]

The important matter of determining oxygen in certain organic substances is again dealt with by a modification of the catalytic hydrogenation method. The procedure is applied to organic compounds containing nitrogen, sulphur and halogens.[79]

Formaldehyde readily reacts with potassium hydrogen sulphite with formation of a neutral sulphonate, so that excess of the reagent may be determined by titration with standard alkali hydroxide.[80] With potassium cyanide, the product first formed is the potassium derivative of glycollonitrile, the hydrolysis of which is accelerated by magnesium sulphate. The excess of cyanide is titrated with silver after the precipitated magnesium hydroxide has been dissolved by addition of ammonium chloride.[81]

The conditions for the determination of tartaric acid in the form of its calcium salt are set out,[82] and this acid may be determined by oxidation with a measured excess of dichromate. The latter method is applicable to sucrose, β-naphthol, salicylic and phthalic acids.[83]

Acetylation of 2 : 4-dichloroaniline, which has already been used by Orton for determining small amounts of acetic anhydride in glacial acetic acid, has now been adapted to the evaluation of the anhydride through the dichloroacetanilide.[84]

A method for the determination of small quantities of lactic acid is based on the formation of acetaldoxime when the acid is distilled with 50% sulphuric acid and the distillate is passed into hydroxylamine.[85] Acetone may conveniently be determined in the presence

[75] H. ter Meulen, *Rec. trav. chim.*, 1925, **44**, 271; *A.*, ii, 599.
[76] *Idem, ibid.*, 1924, **43**, 643; *A.*, 1925, ii, 66.
[77] G. Magnin, *J. Pharm. Chim.*, 1925, [viii], **1**, 333; *A.*, ii, 594.
[78] G. Newbery, *J.*, 1925, **127**, 1751.
[79] H. ter Meulen, *Rec. trav. chim.*, 1924, **43**, 899; *A.*, 1925, ii, 156.
[80] G. Romeo, *Ann. Chim. Appl.*, 1925, **15**, 300; *A.*, ii, 1009.
[81] E. Schulek, *Ber.*, 1925, **58**, [*B*], 732; *A.*, ii, 606.
[82] M. François and C. Lormand, *J. Pharm. Chim.*, 1924, [vii], **30**, 276; *A.*, 1925, ii, 75.
[83] K. Täufel and C. Wagner, *Z. anal Chem.*, 1925, **67**, 16; *A.*, ii, 1007.
[84] W. S. Calcott, F. L. English, and O. C. Wilbur, *Ind. Eng. Chem.*, 1925, **17**, 942; *A.*, ii, 1007.
[85] P. Leone and G. B. Tafuri, *Ann. Chim. Appl.*, 1925, **15**, 206; *A.*, ii, 907.

of alcohol by a vapour pressure method,[86] whilst the 2 : 4-dinitrophenylhydrazone may be used for the determination of very small quantities in urine.[87]

Directions are given for the elimination of the interfering cyanamide derivatives in the determination of cyanamide,[88] the calcium compound of which can be assayed by treatment, after hydrolysis, with methylxanthhydrol, whereby xanthylcarbamide is produced and weighed.[89]

The requisite conditions for the determination of oleic acid by conversion into dihydroxystearic acid have now been worked out.[90]

Cinchonine as a tannin precipitant is of particular value in the analysis of cutch and gambier, since the catechin, which is largely absorbed by hide powder, is not affected.[91]

From a potentiometric study of the titration of various alkaloids, methyl-red is recommended as indicator for strychnine, brucine, morphine, codeine, nicotine, hydrastine, atropine, and cinchonine; methyl-orange for narcotine; and *p*-nitrophenol for quinine, with appropriate buffer solutions in the last three instances.[92] Similar results for some other alkaloids are given elsewhere.[93] Mixtures of morphine, narcotine, and codeine, titrated with silicotungstic acid by a conductometric method, give curves showing points of inflexion corresponding with successive precipitation of the alkaloids.[94]

Novocaine may be determined colorimetrically in the presence of several allied substances, by the colour formed on mixing with solutions of sodium nitrite, hydrochloric acid, and sodium carbonate containing potassium guaiacolsulphonate; sodium hydrogen sulphite should be removed before diazotising.[95] The blue condensation product with vanillin given by trytophan in presence of concentrated hydrochloric acid may be applied to determination of the amino-acid.[96] A filtered acid extract of suprarenal powder mixed with solutions of sodium acetate and mercuric chloride produces in the presence of adrenaline a red coloration which can serve for colorimetric comparison with a standard solution of adrenaline.[97]

[86] E. A. Vuilleumier, *Ind. Eng. Chem.*, 1925, **17**, 174; *A.*, ii, 246.
[87] C. Bülow, *Science*, 1925, **61**, 344; *A.*, ii, 1210.
[88] L. A. Pinck, *Ind. Eng. Chem.*, 1925, **17**, 459; *A.*, ii, 607.
[89] R. Fosse, P. Hagene, and R. Dubois, *Compt. rend.*, 1924, **179**, 408; *A.*, 1925, ii, 76
[90] A. Lapworth and E. N. Mottram, *J.*, 1925, **127**, 1628.
[91] D. Hooper, *Analyst*, 1925, **50**, 162; *A.*, ii, 443.
[92] H. B. Rasmussen and S. A. Schou, *Pharm. Zentr.*, 1924, **65**, 729; *A.*, 1925, ii, 247.
[93] F. Müller, *Z. Elektrochem.*, 1924, **30**, 587; *A.*, 1925, ii, 607.
[94] F. E. Raurich Sas, *Anal. Fis. Quím.*, 1925, **23**, 277; *A.*, ii, 1011.
[95] P. Cheramy, *J. Pharm. Chim.*, 1924, **30**, 408; *A.*, 1925, ii, 247.
[96] I. Kraus, *J. Biol. Chem.*, 1925, **63**, 157; *A.*, ii, 448.
[97] O. Bailly, *J. Pharm. Chim.*, 1924, **30**, 404; *A.*, 1925, ii, 248.

A procedure devised to fulfil conditions considered best is described for the determination of the copper number in the chemical analysis of cotton,[98] also a method to circumvent the fact that copper numbers obtained from alkali-soluble celluloses by Schwalbe's method are not comparable with values similarly obtained from alkali-insoluble celluloses, on account of the sensitiveness of the former to the action of hot alkali.[99]

Since appreciable errors may be incurred in the volumetric determination of reducing sugars on account of copper sulphate pentahydrate containing excess of moisture, Fehling's solution should be standardised against invert-sugar.[1] Superheating causes an error which may be avoided by addition to the mixture of Fehling's solution and assay liquid of an inert powder to promote regular ebullition.[2]

Possible errors in Schoorl's method for the determination of invert-sugar in liquids containing sucrose have been investigated; allowance must be made for the fact that the sucrose reduces Fehling's solution to an extent diminishing with increasing quantities of this compound.[3] Modifications have also been made by the author of the method.[4]

All carbohydrates, etc., that give hexoses on hydrolysis yield, on distillation with 12% hydrochloric acid, hydroxymethylfurfuraldehyde, so that the determination of pentosans by this method may lead to erroneous results. A procedure for regulating the distillation so as to yield fairly good results is given in some detail.[5] A lengthy paper deals with the determination and formation of hydroxymethylfurfuraldehyde.[6]

The influence of a number of substances such as chlorides and alkaline earths on the reducing action of dextrose has been investigated,[7] and the interaction of dextrose and methylene-blue has been placed on a quantitative basis.[8]

Two descriptions of methods for the determination of chlorine in benzaldehyde are given, one using a bomb calorimeter for the com-

[98] D. A. Clibbens and A. Geake, *J. Text. Inst.*, 1924, **15**T, 27; *A.*, 1925, ii, 906.

[99] K. Hess, *Annalen*, 1924, **440**, 290; *A.*, 1925, ii, 245.

[1] J. H. Lane and L. Eynon, *J. Soc. Chem. Ind.*, 1925, **44**, 150T; *A.*, ii, 445.

[2] L. Pick, *Z. Zuckerind. Czechoslov.*, 1925, **49**, 211, 219, 235, 243; *A.*, ii, 906.

[3] M. A. H. van den Hout, P. A. Neeteson, and A. L. van Scherpenberg, *Chem. Weekblad*, 1924, **21**, 578; 1925, **22**, 126; *A.*, ii, 74, 445; C. J. de Wolff, *ibid.*, 78; *A.*, ii, 245; C. van der Hoeven, *ibid.*, 79; *A.*, ii, 331.

[4] N. Schoorl, *ibid.*, 132, 285; *A.*, ii, 445, 828.

[5] F. W. Klingstedt, *Z. anal. Chem.*, 1925, **66**, 129; *A.*, ii, 720.

[6] E. Troje, *Z. Ver. Deut. Zucker Ind.*, 1925, (828), 635; *A.*, ii, 1210.

[7] P. Fleury and P. Tavernier, *Bull. Soc. Chim. biol.*, 1925, **7**, 331; *A.*, ii, 605; L. Rosenthaler, *Pharm. Zentr.*, 1925, **66**, 517; *A.*, ii, 1006.

[8] E. Knecht and E. Hibbert, *J. Soc. Dyers Col.*, 1925, **41**, 94; *A.*, ii, 605.

bustion,[9] the other involving the gradual distillation of comparatively large quantities of the aldehyde from nitrosulphuric acid.[10] Both methods claim great accuracy.

Methods are described for the analysis of various mixtures of phenol nitration products. These depend upon the bromine absorbed and on the formation of nitron picrate.[11]

Aqueous solutions of aniline may be titrated with 0·1*N*-sulphuric acid, using bromophenol-blue, *p*-dimethylaminoazobenzene, or Congo-red as indicator, the first being best. With the toluidines, results are less satisfactory.[12]

An extensive and detailed review has been made of many methods of determining vanillin, piperonal, and coumarin when alone or in admixture.[13]

As the result of a critical investigation of the Höchst test for determination of anthracene, revised directions are now given.[14] Anthracene may be determined in anthraquinone by a colorimetric comparison of the charring which occurs on heating anthracene with oleum, the comparison being made with colour standards prepared from potassium dichromate and cobalt chloride.[15]

Physical Methods.

From a consideration of the absorption constants of the two tautomeric forms of an indicator assumed to be in equilibrium and of the ionic dissociation of the indicator, it is concluded that where the p_H value is not extremely small, it should be a simple function of the absorption ratio and independent of the concentration of indicator, so that a tedious calibration is unnecessary. This is found to be the case with so-called "normal" indicators such as cresol-red and bromothymol-blue; crystal-violet and methyl-red, however, are classed as "abnormal," in that there is a marked deviation from the simple relationship expected.[16] Work on the "apparent" dissociation constants of indicators has been extended to thymol-blue, bromocresol-green, and sodium α-naphthol-2-sulphonate indophenol.[17]

[9] J. D. Bukschnewski, *Z. angew. Chem.*, 1925, **38**, 723; *A.*, ii, 1000.

[10] T. H. Faust and T. Spängler, *Chem. Ztg.*, 1925, **49**, 724; *A.*, ii, 1000.

[11] L. Desvergnes, *Ann. Chim. Analyt.*, 1925, [ii], **7**, 35, 65, 97; *A.*, ii, 447, 607.

[12] C. M. Carson, *Ind. Eng. Chem.*, 1925, **17**, 62; *A.*, ii, 447.

[13] L. G. Radcliffe and E. H. Sharples, *Perf. Ess. Oil. Rec.*, 1924, **15**, 396, 437; 1925, **16**, 20, 51, 87, 156, 197, 271, 353, 387; *A.*, ii, 1210.

[14] F. H. Rhodes, M. L. Nichols, and C. W. Morse, *Ind. Eng. Chem.*, 1925, **17**, 839; *A.*, ii, 1005.

[15] H. P. Lewis, *ibid.*, 1924, **16**, 1184; *A.*, 1925, ii, 74.

[16] F. Vlès, *Compt. rend.*, 1925, **180**, 584; *A.*, ii, 595. Compare W. R. Brode, *Ann. Report*, 1924, **21**, 152.

[17] W. C. Holmes and E. F. Snyder, *J. Amer. Chem. Soc.*, 1925, **47**, 221, 226, 2232; *A.*, ii, 325, 999.

The spectrophotometric method has been examined with the idea of utilising the method as a quantitative measure of substances oxidisable by potassium permanganate.[18] The blue colour obtained with hydrochloric acid and solutions of cobalt is due to an absorption spectrum of four bands, easily perceptible at great dilution with a direct-vision spectroscope. This has been utilised to determine traces of cobalt in nickel salts.[19]

Traces of gold, down to 10^{-4}%, in minerals or isolated by appropriate means from solutions, may be detected by an examination of the arc and spark spectra. The line 2428·1 Å. is considered the most suitable line of the spark spectrum for the detection of gold.[20] Quantitative methods of analysis with the aid of *X*-rays are described. One method takes account of the relative intensities of the photographed spectrum lines;[21] another is a modification of the method of determining the proportion of a metal in a mixture of oxides containing it by adding known weights of another oxide until the intensity of one of its lines in the *X*-ray spectrum coincides with that of the corresponding line in the spectrum of the metal the proportion of which it is desired to determine.[22] This procedure has been utilised to determine hafnium in zirconium materials, or zirconium in hafnium compounds.

A strong collodion diaphragm, resistant to a pressure of 40 atmospheres, is described for physico-chemical analysis of solutions. It is built up of fine wire, surrounding an artificial silk envelope, which in turn covers an enamelled metal tube pierced by small holes.[23] At great dilutions, proteins such as egg-albumin will prevent the lowering of the surface tension of water by sodium oleate, and this may be utilised for detecting minute quantities of proteins in solution.[24]

When a solution containing sodium hydrogen tartrate and ammonium molybdate is treated with a potassium salt, the reaction of the latter with the tartrate results in depression of the optical rotation of the liquid, the extent of this depression serving as a means of determining the amount of potassium added.[25]

Additional mixtures of thallium salts (formate, malonate, and fluoride) have been prepared which allow of the separation of minerals of all specific gravities between 1 and 5·4.[26]

[18] H. Gombos, *Biochem. Z.*, 1924, **151**, 1; *A.*, 1925, ii, 237.
[19] G. Denigès, *Compt. rend.*, 1925, **180**, 1748; *A.*, ii, 826.
[20] P. Joliboisand R. Bossuet, *Bull. Soc. chim.*, 1925, [iv], **37**, 1297; *A.*, ii, 1208.
[21] P. Günther and G. Wilcke, *Annalen*, 1924, **440**, 203; *A.*, 1925, ii, 237.
[22] D. Coster and Y. Nishina, *Chem. News*, 1925, **130**, 149; *A.*, ii, 324.
[23] E. Fouard, *Ann. Chim. Analyt.*, 1925, [ii], **7**, 33; *A.*, ii, 324.
[24] P. L. du Noüy, *Science*, 1925, **61**, 472; *A.*, ii, 1212.
[25] A. Wróbel, *Roczniki Chemji*, 1924, **4**, 287; *A.*, 1925, ii, 240.
[26] E. Clerici, *Atti R. Accad. Lincei*, 1925, [vi], **1**, 329; *A.*, ii, 594.

Electro-chemical Methods.

Electrolytic.—An economic rotating anode of thin platinum wire on a glass stirrer is described, which, although unsuited to methods in which lead is deposited on the anode as peroxide, can be used under proper conditions for the successive deposition of copper and lead in the metallic state. Attention is directed to the unsuitability of anodes of large surface and oxidising power in certain electro-analytical methods.[27] Further work has been carried out on the use of graded potentials for the electrolytic separation of various metals.[28]

The solvent action of nitrous acid on electro-deposited lead dioxide may be overcome by addition of carbamide towards the end of the simultaneous electrolytic deposition of copper and lead.[29] Conditions have been worked out for the rapid electrolytic separation of tin from tungsten. This important separation is effected in the solution containing excess of alkali sulphide by adding Rochelle salt and potassium hydroxide, followed by hydrogen peroxide and phosphate, and final electrolysis at 60—70°.[30] Copper is separated cleanly from tin, antimony, and lead by the use of nitric and tartaric acids,[31] whilst an adherent deposit of antimony may be obtained from chloride solution in the presence of tartaric acid and hydrazine sulphate.[32]

Indium is deposited from acid or alkaline solutions on a dropping-mercury cathode. The reaction is reversible and requires a cathodic potential of 0·503 volt for deposition of the metal from a molar solution.[33] Nickel may be determined accurately in the presence of chromium and iron from alkaline solution by the addition of ammonium oxalate and ammonium citrate.[34] Under no conditions was it found possible to deposit nickel from oxalate electrolytes without some contamination by organic matter, although, in the case of iron, contamination may be retarded sufficiently to allow of quantitative deposition by the addition of ammonium chloride.[35]

Electrometric.—Numerous papers dealing with electrometric titrations and modifications of the electrometric methods have been published. Several convenient types of calomel electrode have

[27] A. Lassieur, *Bull. Soc. chim.*, 1924, [iv], **35**, 1530; *A.*, 1925, ii, 154.

[28] *Idem*, *Compt. rend.*, 1924, **179**, 632, 827; *Ann. Chim.*, 1925, [x], **3**, 235; *A.*, ii, 159, 328, 711.

[29] H. Biltz, *Ber.*, 1925, **58**, [*B*], 913; *A.*, ii, 715.

[30] A. Jilek and J. Lukas, *Chem. Listy*, 1924, **18**, 205; *A.*, 1925, ii, 242.

[31] *Idem*, *ibid.*, 378; *A.*, ii, 241.

[32] A. Schleicher and L. Toussaint, *Chem. Ztg.*, 1925, **49**, 645; *A.*, ii, 1004.

[33] J. Heyrovský, *Chem. Listy*, 1925, **19**, 168; *A.*, ii, 717.

[34] E. Rousseau, *Chim. et Ind.*, 1925, **13**, 199; *A.*, ii, 441.

[35] P. K. Frölich, *Analyst*, 1925, **50**, 224; *A.*, ii, 604.

recently been described,[36] whilst both hydrogen gas and a calomel cell can be dispensed with by combining a pure graphite electrode with a platinum spiral electrode through a millivoltmeter. The potential is given as + 0·18 volt for 0·01*N*-acid and − 0·73 for 0·01*N*-alkali.[37]

An antimony electrode may be employed where the hydrogen electrode is inadmissible, *e.g.*, in determining free acid in the presence of oxidising agents.[38] The use of two electrodes, polarised by a constant potential of 0·2—1 volt applied with a large resistance in series, is recommended for electrometric analysis, since an abrupt alteration in potential difference occurs at the end-point.[39] Modifications of the application of the three-electrode valve to electrometric work have been made.[40]

A simple differential method of electro-titration consists in division of the solution to be titrated into two parts, platinum wires connected to a millivoltmeter being immersed in each. The two solutions, also connected with a strip of filter-paper, are simultaneously titrated, one burette being always kept 0·2 ml. ahead of the other. At the end-point, the voltmeter readings suddenly attain a maximum, curves for the maximum being unnecessary.[41]

For the potentiometric standardisation of titanous chloride solutions, a solution of copper sulphate, free from iron and of strength determined accurately by electrolytic deposition, is recommended.[42] The method can be applied to the determination of copper in the presence of mercury, lead, cadmium, zinc and arsenic. Titanous chloride titrations, followed potentiometrically, may be applied also to determining vanadium, antimony, uranium, molybdenum, selenium,[43] and indirectly to manganese, *e.g.*, in iron ores.[44] Bismuth solutions can be readily titrated by reduction from the tervalent condition by means of titanous chloride; the best results are obtained in 3% hydrochloric or in acetic acid solution, sodium chloride and tartaric acid being added to prevent precipitation of

[36] C. J. Schollenberger, *Ind. Eng. Chem.*, 1925, **17**, 649; *A.*, ii, 711; H. C. Parker and G. A. Dannerth, *ibid.*, 637; *A.*, ii, 712.

[37] J. C. Brünnich, *ibid.*, 631; *A.*, ii, 711.

[38] I. M. Kolthoff and B. D. Hartong, *Rec. trav. chim.*, 1925, **44**, 113; *A.*, ii, 325.

[39] R. G. van Name and F. Fenwick, *J. Amer. Chem. Soc.*, 1925, **47**, 19; *A.*, ii, 594.

[40] K. G. Goode, *ibid.*, 2483; *A.*, ii, 1196; W. D. Treadwell and C. Paoloni, *Helv. Chim. Acta*, 1925, **8**, 89; *A.*, ii, 595.

[41] D. C. Cox, *J. Amer. Chem. Soc.*, 1925, **47**, 2138; *A.*, ii, 999.

[42] E. Zintl and A. Rauch, *Z. anorg. Chem.*, 1925, **146**, 281; *A.*, ii, 1003.

[43] O. Tomiček, *Chem. Listy*, 1924, **18**, 210, 233; *A.*, 1925, ii, 243.

[44] A. McMillan and W. C. Ferguson, *J. Soc. Chem. Ind.*, 1925, **44**, 141T; *A.*, ii, 441.

basic bismuth chloride and titanic acid, respectively.[45] By appropriate modifications, the method may be applied to the determination of bismuth in the presence of iron, lead, tin, cadmium, and arsenic, but not in the presence of antimony.[46] A similar reduction occurs with gold, which may be determined in presence of mercury, tin, lead, and copper; in presence of iron, a considerable amount of phosphoric acid should be added.[47]

Stannous and antimonious chlorides may be titrated by potassium dichromate in hydrochloric acid solutions, using the oxidation–reduction electrode to indicate the end-point; the antimony may be titrated separately, after addition of mercuric chloride.[48] The iron–dichromate titration is applied to the determination of ferrous and ferric iron in magnetites.[49] The potentiometric determination of chromium and vanadium in presence of each other has been described and applied to the analysis of steel; [50] also to the determination of tervalent cerium by oxidation of the cerous sulphate or chloride in a concentrated potassium carbonate solution. For the latter case, an oxygen-free atmosphere is necessary, and the titration is effected by potassium ferricyanide.[51]

A sudden large change in the potential occurs in the reaction between the halogens and potassium cyanide when the theoretical quantities for the formation of cyanogen halide are present.[52] A solution of mercurous perchlorate gives better results than the nitrate in the titration of chlorides or bromides, using a mercury electrode.[53] Details are given for the electrometric titration of hypochlorous acid, with comparison electrodes of neutral salts or feeble oxidising agents,[54] and of chlorous acid, particularly in presence of the hypochlorous acid.[55]

Curves for the titration of hydrazine salts with bases are very similar to that obtained with ammonium hydrogen sulphate; the reaction of hydrazine with iodine and with potassium bromate was also followed, as well as the complete oxidation of hydroxylamine to nitrate.[56]

[45] E. Zintl and A. Rauch, *Z. anorg. Chem.*, 1924, **139**, 397; *A.*, 1925, ii, 442.
[46] *Idem, ibid.*, 1925, **146**, 291; *A.*, ii, 1004.
[47] *Idem, ibid.*, 1925, **147**, 256; *A.*, ii, 1005.
[48] M. H. Fleysher, *J. Amer. Chem. Soc.*, 1924, **46**, 2725; *A.*, 1925, ii, 243.
[49] H. R. Adam, *J. S. Afr. Chem. Inst.*, 1925, **8**, 7; *A.*, ii, 717.
[50] I. M. Kolthoff and O. Tomiček, *Rec. trav. chim.*, 1924, **43**, 447; *A.*, 1925, ii, 72.
[51] O. Tomiček, *ibid.*, 1925, **44**, 410; *A.*, ii, 716.
[52] E. Müller and A. Schuch, *Z. Elektrochem.*, 1925, **31**, 332; *A.*, ii, 825.
[53] C. Müller and H. Aarflot, *Rec. trav. chim.*, 1924, **43**, 874; *A.*, 1925, ii, 65.
[54] A. Schleicher and L. Toussaint, *Z. anal. Chem.*, 1925, **65**, 399; *A.*, ii, 433.
[55] A. Schleicher and W. Wesly, *ibid.*, 406; *A.*, ii, 433.
[5] E. C. Gilbert, *J. Amer. Chem. Soc.*, 1924, **46**, 2648; *A.*, 1925, ii, 239.

Between the limits p_H 2·05 and 8·0, accurate determinations of the p_H may be much more rapidly made by replacement of the hydrogen of a platinum–hydrogen electrode by quinhydrone added to the solution.[57] The ordinary hydrogen electrode may be replaced by a small platinised platinum cathode set in a solution of which the p_H is required and to which a small polarising current is applied until the evolution of bubbles just commences. This method is particularly advantageous for alkaline solutions.[58] Of a number of metals and oxides tested for suitability to replace gas electrodes in measuring hydrogen-ion concentrations, the most promising were electrodes of tungsten–manganese sesquioxide and platinum–manganese sesquioxide.[59]

J. J. Fox.
B. A. Ellis.

[57] H. Niklas and A. Hock, *Z. angew. Chem.*, 1925, **38**, 407; *A.*, ii, 595.
[58] S. Glasstone, *Analyst*, 1925, **50**, 327; *A.*, ii, 822.
[59] H. C. Parker, *Ind. Eng. Chem.*, 1925, **17**, 737; *A.*, ii, 899.

BIOCHEMISTRY.

Introduction.

The same arrangement of subject matter has been adopted in this Report as in that for the previous year, namely, soil chemistry, plant biochemistry, and animal and general biochemistry. Once more this results in the inclusion in the first part of the Report of much matter that cannot strictly be termed biochemistry; owing to the importance of modern views on the inorganic and physical chemistry of the soil, and the undesirability of separating the discussion of this from that of other branches of soil chemistry, this anomaly is inevitable.

Apart from the appearance of a few papers of outstanding importance, the year under review is not marked by any radical advance in knowledge. No attempt has been made to cover the whole field in detail, but a few of the more important subjects have been selected for special discussion.

The Inorganic Colloids of the Soil.

The Weathering Process.

In recent Reports emphasis was laid on the important part played by the colloidal aluminosilicates in soil phenomena; attention was directed in the Report for 1923 to the work of Bradfield,[1] which showed that this inorganic colloidal material consisted of a definite compound or mixture of compounds and not of a mixture of the hydrates of silica, alumina, and ferric oxide. Evidence of a similar nature was advanced by Gedroiz.[2] Little is known at present with regard to the nature of the chemical reactions involved in the production of natural aluminohydrosilicates from the parent rock in the process of weathering. R. Schwarz and R. Walcker[3] have advanced a theory according to which transition of felspar into kaolinite consists first in the decomposition of the mineral into its components: $K_2O,Al_2O_3,6SiO_2 \longrightarrow 2KOH + 2Al(OH)_3 + 6SiO_2aq$; under special conditions the products reunite to form kaolin or an intermediate product. They show that aluminium hydroxide and

[1] *Ann. Reports*, 1923, **20**, 201.

[2] Editorial Cttee. of the People's Comissariat of Agric., Leningrad, 1922.

[3] *Z. anorg. Chem.*, 1925, **145**, 304; *A.*, ii, 887.

silicic acid in an aqueous medium in the proportion $1Al_2O_3 : 6SiO_2$ precipitate a substance of the composition $Al_2O_3,2SiO_2,2H_2O$, which on keeping becomes similar to kaolin. The most favourable zone of reaction for complete precipitation is at p_H 4·8—5·0. A large excess of silicic acid remains in the solution, since the ratio of alumina to silica in the precipitate is 1 : 2. According to these workers, therefore, the natural formation of kaolin, and therefore probably also of the other aluminium hydrosilicates in soil, is not due to an ionic reaction, but to the mutual coagulation of aluminium hydroxide sol and silicic acid sol. It must be admitted that, although Bradfield's results showed conclusively that the synthetic mixture he used was quite distinct from the natural colloid, the possibility that under suitable conditions the mutual precipitation of alumina and silicic acid might finally result in a definite compound was not tested in his work; the results of Schwarz and Walcker show that this may occur, although it has still to be proved that it actually does so in nature.

It is well known that the type of product produced by weathering is largely dependent on climatic conditions. R. Ganssen has recently published a summary of his views on the nature of the essential reactions involved in the chief types of weathering of aluminosilicate rocks.[4] He distinguishes three main types: "Clay weathering," which occurs under humid conditions in cold and temperate zones. Here the reaction consists, in the case of potash felspar, in the production of a mixture of a zeolitic silicate of the general composition $4—6SiO_2,Al_2O_3,K_2O,mH_2O$ with a kaolinitic silicate, $2SiO_2,Al_2O_3,2H_2O$, together with soluble potassium silicate, $3—6SiO_2,K_2O,nH_2O$, which is washed away and lost. Under semi-humid conditions in temperate and tropical zones, "laterite weathering" occurs. This may be true lateritisation in which the intermediate formation of a zeolitic silicate, $6SiO_2,Al_2O_3,K_2O,nH_2O$, is followed by the complete elimination of silica and potash in the form of soluble potassium silicate, $6SiO_2,K_2O,nH_2O$, leaving behind hydrargyllite, $Al_2O_3,3H_2O$, the end-product of weathering in true laterite soils. Alternatively, "clay laterite" weathering may occur, in which, parallel with the above lateritic process, a part of the felspar is converted into kaolinitic silicate which is not further changed. Finally, there is the type of weathering which occurs in arid and semi-arid zones, termed "hydration-weathering." Here the chemical changes are at a minimum. There is no leaching out of soluble products, and the chief reaction is one of hydration only, the felspar being converted by the addition of water into a

[4] Mitt. aus den Lab. der Preussischen Geolog. Landes anstal., Heft 4, Berlin, 1922.

zeolitic silicate, $6SiO_2,Al_2O_3,K_2O,xH_2O$. In another paper,[5] Ganssen deals with the production of loess soils, where the weathering is of the hydration type. The origin, distribution, and composition of laterites are dealt with in a paper by C. O. Swanson.[6]

The reactive aluminosilicates of the soil differ in many respects from true kaolinite; although there is no evidence for the occurrence of true zeolites in soils and clays, it is clear from recent work that the reactive inorganic colloids of the soil behave in a similar way to zeolites or permutites with regard to the ionic exchange and absorption phenomena which they exhibit. A. Demolon[7] regards the reactive aluminosilicates of quaternary clays as zeolitic silicates with a kaolinic nucleus, thus recalling van Bemmelen's well-known division of the weathered silicates in the soil into " complex A " (decomposable by hydrochloric acid) and " complex B " (not decomposed by hydrochloric acid but decomposed by strong sulphuric acid), the latter being often referred to as of a kaolin-like nature.

A careful study of the process of weathering of granite in the Harz mountains has been carried out by E. Blanck and H. Paterson.[8] From an analysis of the material soluble in hydrochloric acid followed by extraction with soda (" complex A "), they find values for the molecular ratio of $K_2O : SiO_2$ which range from 1 : 1·6 to 1 : 2·9 and show marked fluctuations rather than a continuous graduation as the degree of weathering increases. They conclude that the usually accepted value of 1 : 3 for this ratio in the weathering complex of the soils of temperate regions is not well founded, and that the value of " complex A " and of the molecular ratio of alumina to silica as a means of characterising the type of weathering has been much exaggerated.

Mention may also be made of other papers on the formation and properties of zeolites, clays, and substances with a permutoid structure.[9]

Soil Classification.

In recent years, much attention has been directed to the relation between base exchange in soils and such questions as the formation of alkali soils and soil acidity. No apology is made for again laying emphasis on this aspect of the soil, since there appears to be a growing body of evidence to indicate that many of the most important

[5] *Loc. cit.* [6] *J. Amer. Ceram. Soc.*, 1923, **6**, 1248.
[7] *Compt. rend.*, 1925, **181**, 673; *A.*, ii, 1195.
[8] *J. Landw.*, 1924, **71**, 181.
[9] O. Weigel, *Sitzungsber. Ges. Beforder. ges. Naturwiss. Marburg*, 1924, 73; *A.*, 1925, ii, 709; G. Shearer, *Trans. Ceram. Soc.*, 1923—1924, **23**, 314; *A.*, 1925, ii, 698; H. Kautsky and G. Herzberg, *Z. anorg. Chem.*, 1925, **147**, 81; *A.*, ii, 941; G. N. Ridley, *Chem. News*, 1925, **131**, 305; *A.*, ii, 1130.

chemical and physico-chemical changes in the soil can be satisfactorily interpreted in terms of ionic equilibrium and ionic exchanges associated with the colloids of the soil. K. K. Gedroiz [10] has recently published an interesting paper in which he has shown how the relation between many of the chief soil types can be explained from a consideration of the nature and amount of the exchangeable kations in soils. He divides soils into two main types according to whether they do or do not contain absorbed hydrogen in their absorbing complex. Soils of the latter type, which he terms saturated soils, are further subdivided according to the nature of the exchangeable base. In the tsernosem type, this is mainly calcium with some magnesium; such soils are relatively stable and are but little affected by the peptising or dissolving action of water. When sodium is present in addition to calcium there are three possibilities: (*a*) saline soils ("solontshak") containing dissolved sodium salts in their water; (*b*) alkaline soils ("solonetz"), where, owing to the absence of appreciable quantities of dissolved neutral salts, the exchangeable sodium gives rise to alkali by hydrolysis. When the absorbing complex is saturated with sodium it breaks down readily under hydrolytic influences, so that in the absence of chalk in the soil it gives rise to the third type, (*c*) ("soloti"), in which there has occurred an actual loss of a part of the absorbing complex, to an extent comparable with the alkalinity of the alkaline soil from which it is derived. If, however, chalk is present, this loss does not occur, and as the sodium is removed as carbonate, calcium re-enters into the complex to give a soil not differing markedly from the original soil, from which the alkaline soil was derived by the action of sodium salts.

Soils of the other main group contain absorbed hydrogen in their absorbing complex. They owe their characteristics to the fact that the absorbing complex, when markedly unsaturated with bases, shows a pronounced tendency to decompose and give rise to a complex of a new type; this tendency is, however, not so great as in the case of alkali soils, where all the products of decomposition of the complex may be washed away. Two types are distinguished: (*a*) laterite soils, in which there has been a sharply defined destruction of the absorbing complex throughout the whole depth, with abundant accumulation of alumina and ferric hydroxide, and a marked impoverishment in silicic acid; (*b*) podsols, in which the decomposition of the absorbing complex is confined to the surface layers of the profile, and the impoverishment in silicic acid is less than in the case of laterites.

[10] Nossov Agricultural Experiment Station, Agrochemical Div., Paper No. 38, Leningrad, 1925.

Gedroiz's work refers chiefly to Russian soils, but most of the other recognised soil types can be referred to one of the above divisions or to intermediate stages between them. Another factor that must be taken into account in any complete classification is the amount and character of the soil organic matter; here there are many problems awaiting investigation.

In one respect Gedroiz's views are not quite in accord with those of some other soil investigators. In referring to soils of the first group discussed above as "saturated," he appears to consider that a soil with a neutral or slightly alkaline reaction is free from exchangeable hydrogen. As a matter of fact, the inorganic colloidal matter of the soil can go on taking up bases up to a reaction of p_H 10—11; similarly, a neutral salt will bring about a lowering of p_H in a soil even on the alkaline side of neutrality. As stated in last year's Report,[11] these facts can be explained by assuming that the whole of the exchangeable hydrogen of the soil is replaced only at a p_H of 10—11, and that for the attainment of neutrality it is sufficient for only a fraction of the total exchangeable hydrogen to be replaced by basic kations. This distinction between the meaning of the term "saturated" as originally applied to the soil by Ramann, and its significance according to one modern school of thought, is discussed by H. J. Page and W. Williams in the latter part of a paper dealing with the exchangeable bases of Rothamsted soils.[12]

The Relation between Flocculation and Base Exchange.

The flocculation of clay and soil suspensions and the physico-chemical factors controlling the physical condition of the soil are subjects on which a large amount of work has been carried out during the last twenty or thirty years, and very conflicting views have been advanced regarding the nature of the processes involved. Recent investigations on this subject, however, have to some extent cleared up the difficulties in this field, and have brought the phenomena more nearly into line with modern views on the nature of the reactive colloids of the soil.

The marked variations in the flocculating power of neutral salts according to the valency and atomic weight of the metal of the salt, which were investigated by A. D. Hall and C. G. T. Morrison several years ago,[13] were most exhaustively studied by Gedroiz.[14] The differences observed can be correlated with the very

[11] *Ann. Reports*, 1924, **21**, 177, 183.

[12] *Trans. Faraday Soc.*, 1924, **20**, 1. [13] *J. Agric. Sci.*, 1907, **2**, 244.

[14] Communication 24, Bureau of Agr., Scientific Committee of Main Dept. of Land Organisation, 1915. St. Petersburg.

great variation in the physical state of suspensions of clay, according to the kation with which it is saturated. Clay saturated with calcium is relatively hydrophobic and settles to a compact sediment, whereas clay saturated with sodium is very hydrophilic and produces a very voluminous, jelly-like mass.[15] G. Wiegner [16] has shown, in a paper of outstanding importance, characterised by the elegance of the experimental methods used and by the soundness of its theoretical basis, that a satisfactory and convincing explanation of these phenomena can be found in the variations in the degree of hydration of the kations of the neutral salts used or with which the clay is saturated. The nature of the electrical double layer and the manner in which it is influenced by the hydration of the ions in the outer layer are first considered. When the mobile ions of the outer layer are highly hydrated, they cannot approach so near to the inner layer, so that the effective distance between the two layers is increased and the potential of the inner layer increases. The higher the potential, the greater the stability, so that we should expect the stability of a series of clays to increase in the order

H clay, Cs clay, Rb clay, K clay, NH_4 clay, Na clay, Li clay, and Ba clay, Sr clay, Ca clay, Mg clay,

if we accept the usual order for the hydration of the various ions.

From this it is easily seen that base exchange, by altering the ion in the outer layer, can materially alter the stability of the suspension. We should also expect that the most effective precipitating ions would be those which are least hydrated, since they can get nearer to the inner layer than heavily hydrated ions, and so can lower the potential more. We should expect a lithium clay, for instance, to be flocculated by the other ions in the following order, the least active ones coming first :

$Na^{\cdot}$, $K^{\cdot}$, $NH_4^{\cdot}$, $Rb^{\cdot}$, $Cs^{\cdot}$, $H^{\cdot}$.

The ion in the outer layer determines to a certain extent whether the clay tends to be hydrophobe in character or hydrophile, according as it is hydrated to a lower or greater extent. The difference between univalent and bivalent kations depends, not only on the difference in charge, but also on the difference in their degrees of hydration. These ideas were experimentally tested as follows.

[15] K. K. Gedroiz, *Zhur. Opit. Agron.*, 1924, **22**, 29.

[16] *Kolloid-Z.*, 1925, **36**, Zsigmondy-Festschr., 341; *A.*, ii, 527. For other work on this subject see also G. Wiegner, R. Galley, and H. Gessner, *ibid.*, 1924, **35**, 313; *A.*, 1925, ii, 36; R. Galley, *Helv. Chim. Acta*, 1924, **7**, 641; L. C. Wheeting, *Soil Sci.*, 1925, **20**, 363; R. Ed. Liesegang, *Sprechsaal*, 1923, **56**, 513; O. Nolte and E. Sander, *Land. Vers.-Stat.*, 1924, **102**, 219; E. Ramann, *Soil Sci.*, 1924, **18**, 387; *A.*, 1925, i, 223.

Coagulation experiments were carried out by the ultramicroscopic counting method. The percentage decrease in the number of particles after a given time was determined for five different concentrations of electrolyte. Clays in which the bases had been completely replaced by sodium, ammonium, potassium, and calcium were used. The sensitivity to potassium chloride for the various clays was in the converse order from the above, *i.e.*, the sodium clay required the most potassium chloride for a given reduction in the number of visible particles. The order was the same for calcium chloride, which always flocculated better than potassium chloride.

The determination of the comparative degrees of hydration was carried out using an Ostwald viscosimeter, the assumption being made that the hydration will show itself in increased viscosity. The viscosity rose in the series Ca, K, NH_4 and Na clay, but the rise was not large. A calcium or a potassium clay being used, the time taken to reach a maximum viscosity when coagulation was effected with the same quantity of different chlorides (a quantity insufficient for complete discharge being used) was determined. It was found that the more hydrated was the kation of the clay, the less sensitive was the clay in the region of slow coagulation. The coagulation occurs the more quickly the less hydrated are the coagulating ions so long as they are of the same valency.

Slight traces of alkali hinder the flocculation of clay by neutral salts, although in higher concentrations alkalis have the opposite effect of facilitating flocculation. These facts can be interpreted on the assumption that clays can absorb hydroxyl ions. Such absorption was thought by Michaelis to occur; and in the work of S. E. Mattson, this process is invoked to explain the effect of alkalis on flocculation by multivalent ions. Mattson [17] made the important discovery that in this flocculation there is usually little actual neutralisation of the charge on the particles. Clay particles with absorbed hydroxyl ions are supposed to attract calcium ions, which act as a link between adjacent particles. The floccules thus consist of smaller particles carrying hydroxyl ions and are held together by a sort of cement of calcium ions.

As will be clear in the following discussion on Kappen's views, the reality or not of this postulated ability of soil colloids to absorb hydroxyl ions is a crucial question in judging the rival views regarding the nature of soil acidity. It is much to be hoped that further work on this subject will be forthcoming. If the view of the soil colloids as colloidal aluminosilicic or humic acids is a correct one, it is somewhat difficult to understand why such electronegative acidic material should absorb negative hydroxyl ions; it would in

[17] *Koll. Chem. Beihefte*, 1922, **14**, 227.

many ways simplify matters if the influence of alkalinity on flocculation could be satisfactorily explained purely in terms of the kationic exchange which suffices for most of the other physico-chemical phenomena of soil colloids. Further evidence that the absorption of kations by the soil is to be regarded as a chemical process is afforded by P. N. Pavlov.[18] The absorption of dyes by soils, which has often been proposed as a method of measuring the amount of colloidal matter in the soil, has been shown by J. A. Wilkinson and W. Hoff [19] to partake of the nature of a base exchange between the dyes and the bases in the soil; similarly, the absorption of salts of organic bases by calcium permutite and by clay has been found by E. Ungerer [20] to depend on base exchange. A. M. Smith [21] has published an investigation on the exchangeable bases in some Scottish soils. The importance of exchangeable bases in the soil in relation to the supply of nutrient materials to the plant is well illustrated by the interesting results obtained by A. von Nostitz.[22] It was found that when several agricultural plants were grown in sand cultures they made far better growth when calcium, magnesium, and potassium were supplied in the form of their permutite complexes than when they were supplied as soluble salts.

The Nature of Soil Acidity.

There is no diminution in the bewildering number of papers that are published on soil acidity, and much confusion of thought still exists with regard to this subject. The most prominent German worker on this subject is Kappen, whose views have received wide although not unanimous support in Germany.[23] Kappen distinguishes four types of soil acidity which he appears to regard as distinct phenomena. When a soil becomes sour owing to depletion of lime, the first type of acidity to develop is called by Kappen "hydrolytic acidity." This is manifested by the fact that treatment with sodium acetate solution gives rise to acidity in the liquid. This Kappen explains by assuming that in an only mildly decalcified condition, the soil can take up the base of a hydrolysed salt, leaving the free acid in solution. This it is supposed to do by

[18] *Kolloid-Z.*, 1925, **36**, 78; *A.*, ii, 287.
[19] *J. Physical Chem.*, 1925, **29**, 808; *A.*, i, 1227.
[20] *Kolloid-Z.*, 1925, **36**, 228; *A.*, ii, 658.
[21] *J. Agric. Sci.*, 1925, **15**, 466.
[22] *Landw. Vers.-Stat.*, 1925, **103**, 159.
[23] H. Kappen, *Z. Pflanz. Dung.*, 1924, **3A**, 209; *A.*, 1925, i, 221; H. Kappen and K. Bollenbeck, *ibid.*, 1925, **4A**, 1; H. Kappen and R. W. Beling, *ibid.*, 1925, **6A**, 1; E. Kurckmann, *ibid.*, 1925, **5A**, 1; *A.*, i, 1032; O. Lemmermann, J. Hudig, H. Niklas, O. Nolte, D. J. Hissink, R. Ganssen, and E. Ramann, *ibid.*, 1925, **4A**, 222, *et seq.*

absorbing the hydroxyl ion, which takes the sodium ion with it and thus the equilibrium

$$CH_3{\cdot}CO_2Na + H_2O \rightleftharpoons NaOH + CH_3{\cdot}CO_2H$$

is moved to the right.

The next type of acidity to develop in the soil is called " exchange acidity "; a soil possessing this type of acidity gives an acid solution when treated with a neutral salt, and since, as shown previously by Daikuhara, aluminium is then present in the liquid in an amount sufficient to account for the observed acidity on the assumption that this is due to the hydrolysis of aluminium chloride, Kappen regards this acidity as due to the direct exchange of aluminium with the kation of the neutral salt, this aluminium being present in the soil silicates in the kationic condition. The next and more severe type of acidity to develop is called by Kappen " neutral salt decomposition "; in this case, the addition of a solution of a neutral salt results in a still higher hydrogen-ion concentration, not necessarily accompanied by an equivalent amount of aluminium, especially in the case of humic soils. This is again explained by assuming the absorption of hydroxyl ions, which is supposed to be increased by the presence of the neutral salt; the hydroxyl ion takes the kation of the neutral salt with it, and the hydrogen-ion concentration in the liquid increases accordingly. Finally, " active acidity " develops in a soil entirely depleted of exchangeable bases.

It is to be noted that Kappen and his supporters admit the presence of zeolitic or permutoid aluminosilicates in the soil; moreover, they regard the absorption of hydroxyl ion and kation which they postulate in the case of " hydrolytic acidity " and " neutral salt decomposition " as being merely intermediate to the actual chemical combination of the kation with the silicate. However, they reject the explanation of Hissink and van der Spek [24] and of Gedroiz,[25] according to which, by regarding hydrogen as an exchangeable kation, most of the phenomena of soil acidity can be rationally and simply explained. Although considerable space was devoted to this section of the subject in last year's Report, the persistence in some quarters of views of the type held by Kappen is sufficient excuse for devoting further space to the subject here.

We know that the colloidal matter of soils has a definite affinity for kations, and a tolerably well-defined saturation capacity; moreover, the lower the degree of saturation with basic kations, the more acid is the soil. The work of Bradfield has provided

[24] D. J. Hissink and J. van der Spek, *Chem. Weekblad*, 1925, **22**, 500; *A.*, i, 1525; J. van der Spek, *Onderzoekingen der Rijkslandbowproefstations*, 1922, 162; D. J. Hissink, *Z. Pflanz. Dung.*, 1925, **4A**, 137; *A.*, i, 490.

[25] *Zhur. Opit. Agron.*, 1924, **22**, 3.

strong reasons for regarding the colloidal matter of the soil as truly acidic in nature.[26] Since this colloidal acid exists in the gel form on the surface of soil particles, we cannot apply ordinary stoicheiometric formulæ to the whole system of aluminosilicic acids and associated kations. It is, however, possible to represent the condition at varying degrees of saturation of the acid of the colloid on a percentage basis. Thus if $x\%$ of the total saturation capacity of a colloidal acid is neutralised by basic kations, we may write this as [complex] $\overset{x\mathrm{R}^{\cdot}}{(100\text{-}x)\mathrm{H}^{\cdot}}$; the whole range between complete saturation and complete desaturation is represented by

$$[\text{Complex}]\ 100\ \mathrm{R}^{\cdot} \rightleftharpoons [\text{Complex}]\ \overset{x\mathrm{R}^{\cdot}}{(100\text{-}x)\ \mathrm{H}^{\cdot}} \rightleftharpoons [\text{Complex}]\ 100\ \mathrm{H}^{\cdot}.$$

The left-hand formula corresponds to the "normal" salt, the right-hand one to the free acid, and the intermediate formula to the wide range of "acid salts." We know that the state of complete saturation corresponds to a high p_{H} value of about 10 or 11 and that complete desaturation corresponds to a low p_{H} of the order of 3·5—4. The higher the value of x the higher is the p_{H}. When R is calcium, Hissink's results indicate that neutrality, p_{H} 7, corresponds to a value of about 55 for x for many soils. The different forms of soil acidity of Kappen can be rationally explained in terms of the variation of the value of x in the above formula. The higher the value of x, the smaller will be the percentage of hydrogen in the complex which is capable of exchange with other kations, and hence the lower will be the equilibrium concentration of hydrogen ion in the liquid when the soil is treated with a soluble salt. Hence in a soil with a comparatively small proportion of acidic hydrogen in the colloidal phase, the salt of a "strong" acid such as hydrochloric acid could only bring about a minimal amount of ionic exchange between the kation and this ionic hydrogen, since a very small amount of titratable acidity in the form of hydrochloric acid would be sufficient to give rise to the small equilibrium concentration of hydrogen ion in the liquid. By using the sodium salt of a weak acid, however, considerably more acidic hydrogen can be exchanged for sodium before the same hydrogen-ion concentration is reached in the liquid, since this concentration represents a much higher titratable acidity in the case of a weak acid like acetic acid. Only in the case of more highly desaturated soils, in which the value of x is much lower, is the amount of acidic hydrogen in the colloid high enough for ionic exchange with the salt of a strong acid like

[26] *Ann. Reports*, 1924, **21**, 175. See also W. H. Pierre, *Soil Sci.*, 1925, **20**, 285; *A.*, i, 1526; A. de Dominicis and S. Dojmi, *Annal. Chim. Appl.*, 1925, **15**, 183.

hydrochloric acid to give an appreciable titratable acidity. Kappen's distinction between exchange acidity and neutral salt decomposition rests mainly on the production of soluble aluminium in the former case.[27] The arguments used by Kappen against the view that this aluminium arises as a result of secondary reactions are not very convincing. Space does not allow for a detailed discussion of this side of the question, which will be dealt with by the Reporter elsewhere, but granting such secondary reactions in the production of soluble aluminium it is clear that the various forms of acidity defined by Kappen can be consistently and simply explained as being all manifestations of the same acidic property of the soil colloids, differing only in degree and not in nature. It seems unnecessary to resort to somewhat complicated explanations involving the affinity of an electronegative colloid for the negative hydroxyl ion, when the known affinity of the colloid for positive kations, whether metallic or hydrogen, suffices to explain the phenomena.

In practice, one of the most important requirements is to determine the amount of lime that must be added to render a sour soil suitable for crop-growth—that is to say, its so-called "lime requirement." As pointed out last year,[28] this is by no means synonymous with the amount of lime required to bring the soil to neutrality. Further evidence has been advanced that in many cases the harmful effects of soil sourness are due to deficiency of calcium rather than to actual acidity.[29] Moreover, some workers hold the view that the presence of soluble aluminium may be responsible for infertility in some cases (see below). In such cases, the lime requirement from the agricultural point of view is the amount of lime needed to remedy the lime deficiency or to remove soluble aluminium, not to render the soil neutral.

In any case, the amount of base required to bring the reaction of the soil to any given point is determined far less by the actual hydrogen-ion concentration of the soil suspension than by the buffer action of the soil.[30] Hence the study of the titration curves of soil suspensions is of importance. This subject is dealt with together

[27] H. Niklas and A. Hock, *Z. Pflanz. Dung.*, 1925, **5A**, 370; *A.*, i, 1525; A. Sokolov, *J. Landw.-Wissensch. Moskau*, 1924, **1**, 411; L. Smolik, *Compt. rend.*, 1925, **180**, 1773; *A.*, i, 1032.

[28] *Ann. Reports*, 1924, **21**, 183.

[29] A. Densch, Hunnius, and Pfaff, *Z. Pflanz. Dung.*, 1924, **3B**, 248; A. Densch, *ibid.*, 1924, **3A**, 218; *A.*, 1925, i, 221; G. W. Robinson and R. Williams, *Trans. Faraday Soc.*, 1925, **20**, 1; *A.*, i, 222. J. R. Fleetwood, *Soil Sci.*, 1925, **19**, 441.

[30] J. Charlton, *Mem. Dept. Agric. India*, 1924, **7**, 111; *A.*, 1925, i, 768; E. W. Bobko and D. W. Druschinin, *Z. Pflanz. Dung.*, 1925, **5A**, 345; *A.*, i, 1525.

with many other important questions in relation to soil reaction in an interesting series of papers by Crowther [31] which should be read in the original.

Attention may also be directed to several papers dealing with the changes undergone and caused by lime in the soil.[32]

The Influence of Soil Reaction on Plant Growth.

Several papers have been published dealing with the relation between the reaction of the soil and the growth of various agricultural crops. These serve to emphasise the well-known fact that crops vary widely in their sensitiveness to soil acidity. Thus the work of C. Olsen [33] shows that although the optimum range of p_H for lucerne (6·5—7·0) differs but little from that for rye (6·0—6·5) or for buckwheat (6·0—7·0), the first-named crop gives 13% of its optimum growth in a soil of p_H 4·0, whereas buckwheat and rye at this reaction still give 90% and 82%, respectively, of the growth at optimum p_H. Olsen's work also shows in common with that of M. Trénel [34] that the majority of plants prefer a slightly acid or neutral reaction, and that excess alkalinity has a far greater depressing effect than has excessive acidity. O. Arrhenius,[35] who has also investigated the growth of common farm crops in soils of varying reaction, claimed to show that the curves illustrating the relationship between plant growth and the p_H of the soil invariably have two maxima, but Olsen [33] could find no evidence for this in the case of lucerne. Arrhenius [36] could find little evidence that the infertility of acid soils is often due to aluminium, since toxic quantities of this element are usually only detectable in very acid soils. This point has been specially investigated by O. C. Magistad,[37] who has shown that more than three parts of alumina per million can be present in a soil solution only when the reaction is outside the range of p_H 4·7—8·0. Important papers on the effects of soil acidity on plants have also been published by H. Kappen,[38] H. Kirste,[39] and A. Schuckenberg,[40] although in these cases the

[31] E. M. Crowther and W. S. Martin, *J. Agric. Sci.*, 1925, **15**, 237; *A.*, i, 876; E. M. Crowther, *ibid.*, pp. 201, 222, 232; *A.*, i, 875.

[32] F. Scheffer, *J. Landw.*, 1925, **72**, 201; *A.*, i, 624; E. Blanck and W. Lohmann, *Z. Pflanz. Dung.*, 1924, **3A**, 91; *A.*, 1925, i, 223; E. Blanck and F. Scheffer, *ibid.*, 1925, **4B**, 66; *A.*, i, 491; A. Gehring and C. Schulcke, *ibid.*, 113; A. Gehring, *ibid.*, p. 70; W. Renner, *ibid.*, p. 417; A. Gehring and O. Wehrmann, *Landw. Vers.-Stat.*, 1925, **103**, 279; *A.*, i, 1031.

[33] *Compt. rend. Trav. Lab. Carlsberg*, 1925, **16**, 1.

[34] *Z. Pflanz. Dung.*, 1925, **4B**, 340.

[35] *Ibid.*, 1925, **4A**, 30; *A.*, i, 490.

[36] *Ibid.*, p. 348; *A.*, i, 766.

[37] *Soil Sci.*, 1925, **20**, 181; *A.*, i, 1371.

[38] *Z. Pflanz. Dung.*, 1925, **4A**, 202; *A.*, i, 874.

[39] *Ibid.*, 1925, **5A**, 129.

[40] *Ibid.*, 1924, **3A**, 65.

conclusions are somewhat confused by the classification of acidity into different types, as already mentioned on page 201.

R. E. Neidig and H. P. Magnuson [41] have published a series of papers dealing with the relative toxicity of the various salts, commonly found in "alkali soils," to a number of agricultural crops.

Nitrogen and Carbon Cycles in the Soil.

Humic Matter.

Of the many hypotheses that have been advanced with regard to the origin and mode of formation of humic acid, the lignin hypothesis of Fischer and Schrader [42] continues to attract an increasing amount of attention. On the whole, the balance of the evidence appears to be in its favour. One of the principal opponents of this hypothesis is J. Marcusson, who regards oxycellulose as the parent substance of humic acid.[43] The most important argument advanced by him against the lignin hypothesis is based on the fact that sphagnum peat contains more than 40% of humic acid, although the sphagnum from which it is formed is stated to contain very little lignin. This is an argument that cannot be lightly disregarded, and further work on the constituents of sphagnum moss and its humification is badly needed in order to clear up this point.

In another paper, Marcusson [44] advances further arguments in favour of his assumption that humic acid contains furan nuclei. O. Burian [45] also has described experiments purporting to demonstrate the formation of furfuraldehyde from humic acid, but the validity of his methods has been questioned by W. Eller,[46] who reasserts his opinion [47] that artificial humic acids prepared from cellulose are not identical with natural humic acids.

C. Wehmer [48] has advanced further evidence that in the decomposition of lignified tissues by fungi the cellulose disappears and the lignin is converted into humic substances.

Studies of the changes in farmyard manure during maturation and rotting in the soil have been carried out by R. Balks [49] and by E. Bottini,[50] but although they provide interesting data on the relative rates of disappearance of various constituents (pentosans

[41] *Soil Sci.*, 1924, **18**, 449; 1925, **19**, 115; **20**, 376; see also D. Féher and S. Vági, *Biochem. Z.*, 1925, **158**, 357; *A.*, i, 1023.

[42] *Ann. Reports*, 1924, **21**, 172. [43] *Z. angew. Chem.*, 1925, **38**, 339.

[44] *Ber.*, 1925, **58**, [*B*], 869; *A.*, i, 793.

[45] *Brennstoff-Chem.*, 1925, **6**, 52; *A.*, i, 372.

[46] *Ibid.*, p. 55; *A.*, i, 372. [47] *Ann. Reports*, 1923, **20**, 200.

[48] *Brennstoff-Chem.*, 1925, **6**, 101; *A.*, i, 521.

[49] *Landw. Vers.-Stat.*, 1925, **103**, 221; *A.*, i, 1031.

[50] *Annal. Chim. Appl.*, 1925, **15**, 346.

appear to be most rapidly attacked), they do not throw any direct light on the question of the parent substance of humic bodies. Wheeler and his co-workers have published further work on the humic substances (or as they prefer to term them, ulmins) in coal.[51] As investigations on this subject and on soil humic substances proceed, it is probable that an increasing number of points of contact will develop.

In a paper by S. A. Waksman,[52] special attention is directed to the so-called " neutral humus " obtained by neutralisation of the acid filtrate from the main humic precipitate produced when an alkaline soil extract is acidified. This material, which has a high ash content, is soluble in both acids and alkalis. It appears doubtful, however, whether this fraction of the soil organic matter, which occurs in relatively small amounts, is of any great significance, although Waksman attaches some importance to its effects in the soil.

The Carbon–Nitrogen Ratio.

Addition to the soil of carbohydrate material, or generally, of organic substances of high C : N ratio, such as straw, has an important effect on the amount of available nitrogen in the soil and therefore on crop growth.[53] There are good reasons for ascribing this influence to the fact that in the presence of an excess of organic material the soil organisms are in a position to multiply, provided that there is available to them sufficient nitrogen for the synthesis of their cell protoplasm. Further papers on this subject, which serve to strengthen this view, although they bring forward no new facts of outstanding importance, have been published by T. L. Martin,[54] T. L. Lyon, J. A. Bizzell and B. D. Wilson,[55] and Gerlach.[56] In a paper by W. A. Albrecht and R. E. Uhland,[57] attention is directed to the indirect effects of changes in moisture content and aëration induced by a straw mulch, which must be taken into account in their influence on nitrate content in addition to the direct effect of carbohydrate derived from the straw.

Of direct bearing on the relations between carbohydrate decomposition and nitrogen availability in the soil are the results of H. Heukelekian and S. A. Waksman,[58] who have studied the decomposition of cellulose by two typical soil fungi. They found

[51] W. Francis and R. V. Wheeler, *J.*, 1925, **127**, 2236; F. V. Tideswell and R. V. Wheeler, *ibid.*, pp. 110, 125.

[52] *Proc. Nat. Acad. Sci.*, 1925, **11**, 463; *A.*, i, 1528.

[53] *Ann. Reports*, 1923, **20**, 241.

[54] *Soil Sci.*, 1925, **20**, 159; *A.*, i, 1372.

[55] *J. Amer. Soc. Agron.*, 1924, **16**, 396; *A.*, 1925, i, 347.

[56] *Z. Pflanz. Dung.*, 1925, **48**, 534.

[57] *Soil Sci.*, 1925, **20**, 253.

[58] *J. Biol. Chem.*, 1925, **66**, 323.

that the cellulose was completely decomposed by the organisms and could be fully accounted for by the carbon dioxide evolved and the carbon assimilated and built up into fungal tissue. The carbon and the nitrogen assimilation bore a definite relationship to each other. A direct correlation thus exists between the amount of cellulose decomposed and the amount of nitrogen transformed into insoluble organic form.

On the basis of relationships of this sort, Waksman [59] has advanced an interesting explanation of the well-known and striking fact that in most cultivated soils the C : N ratio is relatively constant, seldom showing more than small divergences from a value of about 10. This Waksman explains by supposing that the C : N ratio of the organic matter of the soil, as a product of the action of soil organisms, is controlled by the definite relation between the amount of carbonaceous matter assimilated by the soil organisms and the amount of nitrogen built up into their cells at the same time. Any excess of nitrogen beyond the amount required for the assimilation of the carbon available will be converted into a soluble form and be lost from the soil by leaching or by absorption by the roots of plants. Thus the complete transformation of organic matter added to the soil involves the passage of the whole of the carbon and nitrogen finally appearing as soil organic matter, through the stage of micro-organic cell material of fixed C : N ratio, with the necessary result that the C : N ratio of the whole of the resulting organic matter is fixed within narrow limits. This explanation is, on the face of it, a very attractive one, and it seems almost inevitable that in the process of decomposition of organic matter by soil organisms such regulatory mechanism must operate. This is, however, not the whole story, for no account is taken of the extraordinary stability of the nitrogen compounds of the soil. Despite the presence in the soil of innumerable protein-splitting, ammonifying, and nitrifying organisms, and of conditions favourable to their action, the bulk of the organic nitrogen of the soil is very resistant to degradation. The amount of nitrate and ammonia in the soil is never under ordinary conditions more than a small percentage of the total nitrogen. There are good grounds for believing that most of this nitrogen is present in an unorganised form, *i.e.*, not in the form of cell protoplasm of living organisms, in which condition it would, of course, be immune from extensive breakdown. Yet according to Waksman's hypothesis the nitrogen all passes through the stage of micro-organic protoplasm, and after the death of the

[59] *J. Agric. Sci.*, 1924, **14**, 555.

[60] Compare H. Strache, H. Zikes, and G. Polcich, *Z. Pflanz. Dung.*, 1925, **6A**, 56.

micro-organisms, of protein.[60] Why is this protein not rapidly attacked and broken down to ammonia and nitrate? It is clear that if it persists in the soil in the form of protein it must be protected in some way from the further action of micro-organisms, except at a very slow rate.

Recent work in the Reporter's laboratory at Rothamsted by R. P. Hobson [61] has provided definite evidence for the existence of the greater part of the soil nitrogen in the form of protein; moreover, it has been shown that this protein is associated with the humic matter of the soil. This humic matter as ordinarily prepared always contains about 4% to 5% of nitrogen and has a C : N ratio not far removed from 10. Hitherto the form in which this nitrogen exists has been a matter of much doubt; it was uncertain whether it was an integral constituent of the humic acid molecule or merely present as an associated impurity.

The work of Hobson appears to indicate that the soil contains a humic matter-protein complex of tolerably constant composition. This would explain why the carbon–nitrogen ratio of the soil varies within fairly narrow limits and moreover the association of the protein with the humic matter can easily be conceived as protecting the former in some way from the action of micro-organisms. The small amount of nitrate and ammonia ordinarily present in the soil would represent the breakdown of the small proportion of the total protein liberated by the slow oxidation of the associated humic matter. Much further work is needed before this view can be fully accepted, but it provides a reasonable explanation of the known facts.

Combining this view with that which supposes the origin of humic matter from lignin, we can envisage the course of the conversion of organic residues into soil organic matter as consisting of two converging series of changes. The first consists in the conversion, whether by biological or purely chemical agencies is not yet known, of the lignin in these residues into humic matter; the second involves the conversion of the non-lignin constituents (mainly carbohydrate and protein) into micro-organic protein. The products of these two series then combine to give a humic matter-protein complex which is resistant to biological degradation and of approximately constant composition.

A useful survey of recent work on soil biochemistry is contained in a paper by Waksman [62] based on an extensive tour of most of the laboratories of Europe in which work on soil microbiology is in progress.

[61] Ph.D.(London), Thesis (not yet published).
[62] *Soil Sci.*, 1925, **19**, 201.

The Effect of Soil and Other Factors on Plant Growth.

The Rôle of Silica in Plant Nutrition.

The striking results obtained by Lemmermann in his investigations of the effect of colloidal hydrated silica on the yield of plants grown on media deficient in phosphates have been to some extent explained by further work. It will be remembered that in the Report for 1922 [63] the Reporter questioned the validity of Lemmermann's conclusion that the observed effects of colloidal silica were due to its ability to *replace* phosphates in the plant, and pointed out that analytical data for the relative amounts of silica and phosphoric acid taken up by the plants were required in order to decide the relative merits of Lemmermann's explanation and the one already advanced to account for the older Rothamsted results, according to which the action of silica was an indirect one, in which the phosphate uptake by the plant was increased by the silica. O. Lemmermann, H. Wiessmann, and K. Sammet [64] have now published the results of a further investigation, in which the required analytical results are forthcoming. These show quite definitely that the favourable action of silica is correlated with an increased assimilation of phosphoric acid by the plant. Lemmermann therefore abandons his earlier views, and explains his results by the older hypothesis, to which these later results quite definitely point, namely, that the silica exerts a solvent action on the phosphate present in the soil and renders it more easily available to the plant. His conclusions were criticised by E. Duchon, but Lemmermann in his reply [65] satisfactorily answered these criticisms. Densch [66] and Gile and Smith [67] also have obtained evidence of the action of silica in increasing the availability of phosphates to the plant.[68]

The Influence of Boron on Plant Growth.

The striking work of Miss Warington,[69] which demonstrated the necessity of small traces of boron for normal growth of many leguminous plants, has been extended by Miss W. E. Brenchley and H. G. Thornton.[70] These workers have shown that small traces of boron (1 : 500,000 parts of boric acid) are necessary for the proper

[63] *Ann. Reports*, 1922, **19**, 215.
[64] *Z. Pflanz. Dung.*, 1925, **4A**, 265; *A.*, i, 766; H. Wiessmann, *ibid.*, p. 73.
[65] F. Duchon, *ibid.*, p. 316; O. Lemmermann, *ibid.*, p. 326; *A.*, i, 767.
[66] *Landw. Jahrb.*, 1924, **60**, 142; *A.*, 1925, i, 767.
[67] *J. Agric. Res.*, 1925, **31**, 247.
[68] See also D. R. Nanji and W. S. Shaw, *J. Soc. Chem. Ind.*, 1925, **44**, 1T; *A.*, i, 214.
[69] *Ann. Reports.*, 1923, **20**, 219.
[70] *Proc. Roy. Soc.*, 1925, **98**, *B*, 373; *A.*, i, 1368.

development of root nodules and that in the absence of boron the vascular supply of the nodules is defective. The nodules, instead of supplying nitrogen compounds to the plant, tend to become parasitic, attacking the protoplasm of the host plant.

Stimulants of Plant Growth.

For many years past, somewhat surprising claims have been advanced on the Continent, particularly by Popoff, that considerable increases in the yield of crops could be brought about by treatment of the seeds with a great variety of chemicals. Several papers on this subject have appeared during the past year.[71] If the effects claimed are real, and if they can be cheaply and easily obtained, it would be a matter of considerable economic importance, but at present the evidence cannot be regarded as entirely satisfactory. Many of the experiments demonstrate at the most that improved germination and growth of seedlings results; in the absence of more comprehensive tests, this cannot be accepted as evidence that the yields of the crops at maturity would be similarly improved.

It is claimed that moderate dressings of copper sulphate in the field, or steeping the seed in a weak solution of that salt, produced considerable increases in the yield of barley.[72]

A. Saeger [73] has produced further evidence to that advanced last year by Clark and Roller [74] to show that certain lower plants can be satisfactorily grown for many months on end in a solution of purely inorganic salts. Although evidence was obtained for a stimulation of growth by yeast extract or peat extract,[75] the necessity of organic accessory foods (auximones) for the growth of green plants cannot be regarded as having been proved.

The Effect of Drying the Soil.

A. N. Lebediantzev [76] has carried out a comprehensive series of experiments on the effect on its fertility of air-drying the soil. It has long been known that considerable increase in fertility could result from this treatment. This author's results showed that as an average of 91 pot experiments, a 45% increase in yield of millet was obtained by air-drying a tsernosem soil. The greatest effect was

[71] St. Konsuloff, *Z. Pflanz. Dung.*, 1925, **4B**, 84; H. Lundergardh, *Biol. Zentr.*, 1924, **44**, 465; *Chem. Zentr.*, 1925, I, 2590; T. Bokorny, *Z. Pflanz. Dung.*, 1925, **4A**, 178; *A.*, i, 489; W. Riede, *ibid.*, 1924, **3B**, 533.

[72] Densch, *Landw. Jahrb.*, 1924, **60**, 139; *A.*, 1925, i, 766; A. Densch and Hunnius, *Z. Pflanz. Dung.*, 1924, **3A**, 369; *A.*, 1925, i, 489.

[73] *J. Gen. Physiol.*, 1925, **7**, 517; *A.*, i, 755.

[74] *Ann. Reports*, 1924, **21**, 196.

[75] See also F. A. Mockeridge, *Ann. Bot.*, 1924, **38**, 723; *A.*, 1925, i, 106.

[76] *Soil Sci.*, 1924, **18**, 419.

obtained by repeated drying and rewetting. Chemical analysis showed that there was a marked increase in soluble nitrogen and phosphate content consequent on drying. It is suggested that the effect is akin to partial sterilisation and that the drying of the surface layers of the soil in the field by climatic influences plays a fundamental *rôle* in determining its fertility.

Plant Biochemistry.

The Nitrogen Compounds of Plants.

An exhaustive study of the nitrogen compounds occurring in the rye plant at different stages of ripeness has been made by A. Kiesel.[77] The most noteworthy feature is the high concentration of aspartic acid during the early stages. Asparagine was not found at any stage, and hence it is concluded that aspartic acid is not a forerunner of asparagine. A further study of the proteins of rye may supply the reason for the high content of aspartic acid.

It appears that fungi bear a closer resemblance to animals than to higher plants with regard to the intermediate form in which their nitrogen occurs, since there is evidence that the urea of fungi seems to be the analogue of asparagine in the higher plants, behaving as a waste product in the absence of carbohydrates but as a source of nitrogen for the building up of protein in their presence.[78]

Vickery has published further papers in which is recorded the isolation of a considerable variety of nitrogen compounds from the juice of the lucerne plant.[79]

Jodidi has demonstrated the presence of amino-acids and polypeptides in the ungerminated seeds of several cereals.[80]

Inulin.

H. Colin has shown that the formation of inulin from hexoses in the Jerusalem artichoke occurs mainly in the pith and woody cells of the stem.[81] In other plants, however, such as chicory, the synthesis is confined to the roots.[82] Enzymes are not thought to play any part in the condensation of sugars to the state of lævulosans, and the mechanism of the transformation is unknown.

[77] *Z. physiol. Chem.*, 1924, **135**, 61.

[78] D. Prianischnikov, *Biochem. Z.*, 1924, **150**, 407; *A.*, 1925, i, 213; N. N. Ivanov, *ibid.*, 1924, **154**, 376, 391; *A.*, 1925, 341, 344.

[79] H. B. Vickery and C. S. Leavenworth, *J. Biol. Chem.*, 1925, **63**, 579; *A.*, i, 873; H. B. Vickery, *ibid.*, 1925, **65**, 81; *A.*, i, 1370; H. B. Vickery and C. G. Vinson, *ibid.*, p. 91; *A.*, i, 1370; H. B. Vickery, *ibid.*, p. 657.

[80] S. L. Jodidi, *J. Agric. Res.*, 1925, **30**, 587; *A.*, i, 1027; S. L. Jodidi and J. G. Wangler, *ibid.*, p. 989; *A.*, i, 1224.

[81] *Compt. rend.*, 1924, **179**, 1186; *A.*, i, 620.

[82] *Idem, Bull. Soc. Chim. biol.*, 1925, **7**, 173; *A.*, i, 618.

Pectin.

According to F. W. Norris and S. B. Schryver,[83] pectinogen, which is converted into pectic acid by the action of lime-water, occurs in the plant as a methylated pectic acid in loose combination with metallic ions such as calcium, with one of its four carboxyl groups unmethylated. M. H. Carré [84] contests Tutin's assertion that "protopectin" does not exist, and considers that it occurs in apple tissue, being converted into soluble pectin by hydrolysis. A pectic substance has been obtained from beech-wood by M. H. O'Dwyer.[85] Tutin has shown that the leaves of apples affected with "silver leaf" disease are deficient in pectin in comparison with healthy leaves.[86] A study of the pectin of the peel of citrous fruits has been made by H. D. Poore.[87]

Plant Phosphatides.

V. Grafe and V. Horvat [88] have isolated from the juice of the sugar beet a water-soluble phosphatide giving oleic and palmitic acids, choline and glycerophosphoric acid on hydrolysis, and with a N : P ratio of 1 : 2. From a study of the phosphatides of the soya bean, P. A. Levene and I. P. Rolf [89] find that the lecithin of this plant contains less saturated fatty acids than animal lecithin; it contains, in addition to palmitic and stearic acids, oleic, linolic, and linolenic acids, and also possibly hydroxy-fatty acids. The cephalin of soya beans, however, did not differ appreciably from the animal product.

The Absorption of Ions by Plants.

D. R. Hoagland and A. R. Davis [90] have published an interesting paper, summarising the results obtained in the laboratory of Plant Nutrition of the University of California in a series of investigations on the absorption of ions from dilute solutions resembling soil solutions, and discussing some of the problems arising out of this work. The interesting results obtained in the study of the fresh-water alga *Nitella*, already discussed in an earlier Report,[91] afford a striking illustration of the diffusion of ions from a solution of low concentration to one of higher concentration. If the second law of thermodynamics applies in such cases, this diffusion against the concentration gradient can come about only by virtue of work done within the plant cell. In conformity with this, it was found that

[83] *Biochem. J.*, 1925, **19**, 676; *A.*, i, 1226. [84] *Ibid.*, p. 257; *A.*, i, 758.
[85] *Ibid.*, p. 694; *A.*, i, 1225. [86] *Ibid.*, p. 414; *A.*, i, 1028.
[87] *U. S. Dept. Agric. Bull.*, 1323, pp. 1—19; *A.*, i, 619.
[88] *Biochem. Z.*, 1925, **159**, 449; *A.*, i, 1522.
[89] *J. Biol. Chem.*, 1925, **62**, 759; **65**, 545; *A.*, i, 487, 1520.
[90] *New Phytologist*, 1925, **24**, 99. [91] *Ann. Reports*, 1923, **20**, 225.

there is a definite correlation between absorption of ions and degree of illumination, and it seems probable that energy derived from sunlight is indirectly involved in the absorption processes. Energy required by root cells for these purposes would, of course, be derived from carbohydrates synthesised in the green parts of the plant. The above phenomenon only obtains so long as the living cell is uninjured.

These living plant cells thus appear to possess the property of one-way permeability.

It is impossible to obtain uncontaminated cell sap from higher plants, but the observations that have been made on expressed juices are indicative of a condition which is quite analogous in several respects to that which exists in *Nitella*. The total ion concentration of the tissue fluids of the roots of barley, and still more of the stem and leaves, is much greater than that of the solution in which the barley is grown.

Many erroneous ideas have been held regarding the selective action of plants. It is certainly not true that a plant necessarily selects from a solution only, or even chiefly, those ions indispensable to its growth. Many unessential ions may be absorbed very readily; chlorine, although unessential, is absorbed much more readily than sulphate, which is essential. The same may apply to sodium in comparison with calcium. Although the absorption of the two oppositely charged ions of a salt is often far from equal, this occurs mainly as an ionic exchange, not by large alterations in hydrogen-ion concentrations which are necessarily self-limited. Thus when any considerable excess of potassium ion is removed from a solution of a single potassium salt, other kations such as calcium and magnesium appear in the solution.

However, one ion may markedly affect the absorption of another ion, whether of opposite sign, as evidenced by the much slower uptake of potassium from potassium sulphate than from the chloride, or of the same sign, as when the absorption of calcium or potassium is retarded by the presence of sodium, or when the absorption of nitrate ions is hindered by the presence of chlorine ions.

The relation of ion absorption to transport of water is also of great interest. Water may be absorbed either more or less rapidly than the ions present in the solution. An adequate supply of phosphate may be obtained from a solution of very low phosphate-ion concentration without a proportionate absorption of water. In the words of the authors, " It is equally incorrect to consider the plant either as an organism carefully selecting only the essential ions from a culture medium or as a sort of wick, taking up the solution, evaporating the water, and leaving the solutes behind."

There is evidence that the reaction of the medium may have an important effect on the absorption of ions.

There are many instances to show that anions may be more readily absorbed from an acid solution and kations from an alkaline one.

The reaction of the medium, however, may have very little effect on that of the cell sap of the plant.

It has been shown that equally good growth of plants can be obtained from many culture solutions of widely varying composition. Not only is the plant not dependent on a culture solution of narrowly restricted ionic proportions, but also wide variations are permissible in the concentration.

Since the composition of the medium is one of the primary considerations involved in determining the composition of the plant, it is evident that the latter, in the case of ordinary soil experiments, cannot be used as a means of deciding whether a given species has a characteristic composition. This can only be determined by the comparison of different plants grown under the same conditions in the same culture solution; scarcely any data of this sort are available.

Among the many problems arising out of a consideration of the absorption and utilisation of ions by plants, special attention is directed to such questions as the influence of potassium on the transformations of the organic constituents; the relative parts played by different ions in the buffer system of the plant; the importance of ion-protein relations in the plant cell.

Other recent papers on the absorption of ions by plants are noted below.[92]

Biochemistry of Animals.

Fat-soluble Vitamins.

In last year's Report the author made brief reference to the influence of ultra-violet radiation on calcium metabolism, but in view of the apparently widely conflicting statements that had then been made in various quarters it was, at the time, considered the wiser course to defer further discussion of the matter until more light had been thrown on the nature of the changes concerned. Last year much of the needed information was supplied, so that the subject now seems to be suitable for review.

It will be recalled that in two directions there seemed to be a connexion between ultra-violet radiations and the vitamins. In

[92] J. G. Wood, *Austral. J. Exp. Biol. Med. Sci.*, 1925, **2**, 45; *A.*, i, 1024; G. André and E. Demoussy, *Compt. rend.*, 1925, **180**, 1052; *A.*, i, 758; H. Lundegårdh and V. Morávek, *Biochem. Z.*, 1924, **151**, 296; *A.*, i, 214; E. S. Dowding, *Ann. Bot.*, 1925, **39**, 459; *A.*, i, 871.

the first place, the original observations of Huldchinsky,[93] followed by the work of Hess [94] and the extensive researches of Miss Chick and her colleagues in Vienna,[95] had proved conclusively that rickets could be cured as effectively by exposure to the short-wave radiations of the quartz mercury-vapour lamp as by the administration of anti-rachitic foods, *e.g.*, cod liver oil, whilst, secondly, stimulation of growth in animals deprived of vitamin-*A* had been observed to follow exposure to the radiations.[96]

The natural tendency at first was to believe that the radiations had brought about a synthesis of the active substances in the tissues of the exposed animals, but this belief was disturbed by the claim of Hume and Henderson Smith [97] that a resumption of growth of animals fed on the deficient diets could be brought about merely by placing them in vessels containing air that had previously been exposed to the rays. For a time Webster and Hill's [98] failure to confirm these experimental results was no less confusing than the announcement by Steenbock and Black [99] that food deficient in the fat-soluble vitamins may have growth-promoting and calcifying properties conferred on it by exposure to ultra-violet light.

Chick and Tazelaar [1] showed that the effect noted by Hume and Smith could not be attributed to ionisation of the air, but the first clue to the cause of the discrepancy between the results of the latter investigations and those of Webster and Hill was provided by the demonstration that the growth-promoting and anti-rachitic properties of the contents of vessels irradiated prior to occupancy by the animals resided not in the air but in the sawdust employed for bedding, which the animals ate.[2]

Similar conclusions were reached by Nelson and Steenbock after making an exhaustive investigation of the problem.[3] Confirmation that foods deficient in the growth-promoting vitamin-*A* and the anti-rachitic vitamin-*D* were, after exposure to the short wave-length light of the quartz mercury-vapour lamp or carbon arc, capable of restoring growth and curing rickets was soon forthcoming.[4]

[93] *Deutsch. Med. Woch.*, 1919, **45**, 712.
[94] *Proc. Soc. Exp. Biol. Med.*, 1921, **18**, 298.
[95] Medical Research Council, Report No. 77, 1923.
[96] Hume, *Lancet*, 1923, ii, 1318.
[97] *Biochem. J.*, 1923, **17**, 364.
[98] *Ibid.*, 1924, **18**, 340; *A.*, 1924, i, 789.
[99] *J. Biol. Chem.*, 1924, **61**, 405; *A.*, 1924, i, 1272.
[1] *Biochem. J.*, 1924, **18**, 1346; *A.*, 1925, i, 211.
[2] Hume and Smith, *ibid.*, p. 1334; *A.*, 1925, i, 211.
[3] *J. Biol. Chem.*, 1925, **62**, 575.
[4] Hess and Weinstock, *ibid.*, 1924, **62**, 301; 1925, **63**, 297; *A.*, 1925, i. 212, 750.

The next step was to discover how the "activated" foodstuffs exerted their physiological action.

According to one theory the treated materials emitted secondary radiations that exerted the curative action; a view that was to a large extent based on the claim by Kugelmass and McQuarrie that anti-rachitic substances such as cod liver oil emit a radiation capable of "fogging" a photographic plate after passing through quartz.[5] Drummond and Webster showed that the experiments on which this view was based were faulty,[6] and shortly afterwards Kugelmass and McQuarrie admitted their error.[7]

According to a more attractive hypothesis, physiologically active substances are produced from inactive precursors in the foods by photochemical action of the radiations. Evidence in support of this view has gradually been forthcoming, and its unfolding constitutes one of the most remarkable series of events in modern biochemistry. The precursor of the active substances found in foodstuffs on exposure to ultra-violet light was first traced to the oils and fats present, and finally identified with the sterols phytosterol and cholesterol.[8, 9, 10, 11]

According to Hess and Weinstock, irradiation of cholesterol at first increases the amount of light transmitted, but this effect is reversed on prolonged treatment, and they trace a parallel change in the anti-rachitic potency. Cholesterol and phytosterol undergo marked chemical changes on exposure to ultra-violet light, being converted into pale yellow, waxy products with melting points greatly below those of the original materials. These changes are probably of the same nature as those noted by Schulze and Winterstein [12] in sterols which had been exposed to daylight for long periods, or those caused by *X*-rays.[13] Rosenheim and Webster [14] have shown that the anti-rachitic factor is formed both in presence and in absence of oxygen. Dihydrocholesterol and dihydrophytosterol are not endowed with anti-rachitic potency by treatment with ultra-violet light. The nature of the physiologically active substance (or substances) produced from cholesterol and phytosterol is as yet unknown, but the fact that it can be so readily prepared from these well-known compounds, obtainable in a

[5] *Science*, 1924, **60**, 272.

[6] *Nature*, 1925, **115**, 837; *A.*, ii, 630. [7] *Science*, 1925, **62**, 87.

[8] Hess, Weinstock, and Helman, *J. Biol. Chem.*, 1925, **63**, 305; *A.*, i, 750.

[9] Hess and Weinstock, *ibid.*, 1925, **64**, 181, 193; *A.*, i, 1020.

[10] Steenbock and Black, *ibid.*, p. 263.

[11] Drummond, Rosenheim, and Coward, *J. Soc. Chem. Ind.*, 1925, **44**, 123T; *A.*, i, 617.

[12] *Z. physiol. Chem.*, 1904, **43**, 316; 1906, **48**, 546.

[13] Roffo, *Compt. rend.*, 1924, 180, 228; *A.*, 1925, i, 293.

[14] *Lancet*, 1925, i, 1025.

reasonably pure state, encourages the belief that its identity will not remain long undisclosed.

The first clear proof has been given that the animal organism (rat) possesses the power of synthesising cholesterol.[15] A considerable amount of work had been presented from time to time indicating that cholesterol is synthesised in the bodies of man and animals, *e.g.*, the recent studies of Gardner and Fox [16] on infants, but Channon's carefully controlled experiments decide the matter once and for all.

The elucidation of the action of ultra-violet radiations on cholesterol and closely related sterols has progressed so far that it is evident that it is the anti-rachitic factor (vitamin-*D*), and not the growth-promoting, anti-xerophthalmia vitamin-*A* that is produced.[14] Nevertheless, as an outcome of studies on irradiated food, it has been ascertained that the administration of the anti-rachitic vitamin-*D* can, under certain conditions, induce growth in animals deprived of the fat-soluble vitamins.[17, 18] These facts have necessitated a revision of the methods employed for the testing of materials for the presence of vitamin-*A* by feeding experiments on animals. The new methods not only render obsolete processes which take no regard of the disturbing effects which vitamin-*D* may produce, such, for example, as those recently described by Javillier, Baude, and Lévy-Lajeunesse,[19] and by Sherman and Munsell,[20] or that suggested in the recently issued 7th edition of the American Pharmacopœia, as the method of assay of the growth-promoting potency of cod-liver oil, but also make it clear that a considerable proportion of the work carried out with the older technique will have to be repeated by more trustworthy methods.

Sources of error such as these characterise many biological methods of assay, and serve to direct attention to the pressing need for more accurate and, if possible, more rapid processes. The claim by Drummond and Watson [21] that the long-known colour reaction which cod-liver oils give with sulphuric acid can be taken as an approximate measure of their vitamin potency has not been challenged, although it has not, as yet, received very much attention.[22, 23] Unfortunately, the transient nature of the reaction

[15] Channon, *Biochem. J.*, 1925, **19**, 424; *A.*, i, 1001.
[16] *Proc. Roy. Soc.*, 1925, **98**, *B*, 76.
[17] Steenbock, Nelson, and Black, *J. Biol. Chem.*, 1924, **62**, 275; *A.*, 1925, i. 107.
[18] Drummond, Coward, and Handy, *Biochem. J.*, 1925, **19**, 1068.
[19] *Bull. Soc. Chim. biol.*, 1925, **7**, 831; *A.*, i, 1364.
[20] *J. Amer. Chem. Soc.*, 1925, **47**, 1639; *A.*, i, 1018.
[21] *Analyst*, 1922, **47**, 341.
[22] Poulsson and Weidemann, *Tids. Kemi Bergvaesen*, 1923, **3**, 169.
[23] Sjörslev, *J. Biol. Chem.*, 1924, **62**, 487

renders it useless for the quantitative comparison of different oils, and attempts to stabilise the colour have been unsuccessful. Rosenheim and Drummond [24] have ascertained that a variety of other reagents produce colours similar in character to that produced by strong sulphuric acid, and that their intensities are in a striking manner proportional to the vitamin-*A* potency as determined by feeding experiments on animals. Of the reagents giving colours, the most satisfactory are arsenic trichloride, trichloroacetic acid, and methyl sulphate, and their superiority over sulphuric acid rests on the greater permanence of the colours produced. It was found possible to use the reactions as approximate colorimetric methods of assay of vitamin-*A* with an accuracy at least of the same order as that of the tedious animal tests. The value of these methods as well as that of the colour reactions proposed by Bezssonov [25] as a means of distinguishing the anti-rachitic vitamin from vitamin-*A* is still under consideration.

A group of Japanese investigators has announced the isolation of vitamin-*A* in the pure condition [26] by the distillation of the unsaponifiable matter of cod-liver oil in a high vacuum, after complete removal of cholesterol. The product, for which they propose the name " biosterin," corresponds with the formula $C_{27}H_{42}(OH)_2$, and the presence of one primary alcohol group and three double bonds has been established. Careful perusal of the details of their investigation, however, leaves the impression that their method of separation could not be expected to yield a pure product, and a large proportion of the analytical data for the derivatives, the majority of which were heavy oils, is of questionable value. Many criticisms of the work of Takahashi and his colleagues are contained in a recent paper by Drummond, Channon, and Coward,[27] in which are also described their own attempts to isolate the active substance. Fractions of the same order of physiological activity as those obtained by Takahashi were frequently prepared, but were found to be mixtures. Negative evidence was obtained regarding the identity of vitamin-*A*, in that the following substances, all of which have at one time or another been detected as constituents of unsaponifiable fractions showing physiological activity, were found to be without growth-promoting activity: cholesterol, spinacene (squalene), oleyl alcohol, phytol, batyl alcohol, and selachyl alcohol. A large proportion of the active fractions appears to consist of unsaturated alcohols, so that it is not unreasonable to suppose that vitamin-*A* may be such a substance.

[24] *Biochem. J.*, 1925, **19**, 751.

[25] *Compt. rend.*, 1924, **179**, 572; *A.*, 1925, i, 107.

[26] Takahashi, Makamiya, Kawakami, and Kitasato, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1925, **3**, 81; *A.*, i, 1365.

[27] *Biochem. J.*, 1925, **19**, 1047.

A substance bearing some similarity to vitamins-*A* and -*D* as regards what is known of its chemical behaviour is one now generally referred to as vitamin-*E*. This dietary essential was first described by Evans and Bishop,[28] who found that rats would grow to maturity on a diet containing vitamins-*A*, -*B*, and -*D*, but would not reproduce. Supplementing the diet with certain foodstuffs, *e.g.*, wheat oil, cured the condition. Confirmation of the existence of the newly-discovered factor has been forthcoming,[29, 30, 31] and recently Evans and Burr have provided information concerning its nature.[32] It was found to be stable towards light, heat, acids, alkalis, oxidation and hydrogenation, and it could be concentrated in the unsaponifiable portion of wheat oil without loss. Removal of the cholesterol from this material and distillation of the residue in a high vacuum yielded a fraction of very high physiological activity. Further investigation of this remarkable substance will be awaited with great interest. Meanwhile, it is curious to note how the focus of attention on fats has shifted from the biochemistry of the glycerides to the study of the long-neglected constituents of the unsaponifiable fraction.

With regard to recent proposals for reclassifying the vitamins,[33, 34] Funk's suggestion to subdivide them into two groups, (*a*) vitamins and (*b*) vitasterols, more or less corresponding to the present terms *water-soluble* (*B* and *C*) and *fat-soluble* (*A*, *D* and *E*), seems not only unnecessary but unwise, since it is based on the opinions that the former contain nitrogen and that the latter are sterols. There is no trustworthy evidence that either view is correct, and one is entitled to doubt whether the time is yet ripe for a reconsideration of the nomenclature of these substances.

Chemistry of Internal Secretions.

Parathyroid.—Perhaps the most striking advance that has been made during the past twelve months in the field of research on the internal secretions is the preparation by Collip from parathyroid glands of extracts showing marked physiological activity of the character associated with the gland itself. In last year's Report the author devoted space to the subject of parathyroid tetany, and pointed out that the modern tendency favours the theory that this condition is directly a result of disturbances of the concentration or

[28] *Science*, 1922, **56**, 650.
[29] *Amer. J. Physiol.*, 1923, **63**, 396.
[30] Mattil and Carman, *J. Biol. Chem.*, 1924, **61**, 729.
[31] Sure, *ibid.*, 1924, **62**, 371; *A.*, 1925, i, 212.
[32] *Proc. Nat. Acad. Sci.*, 1925, **11**, 334; *A.*, i, 1022.
[33] Funk, *Bull. Soc. Chim. biol.*, 1925, **7**, 1017.
[34] Randoin and Simonnet, *ibid.*, p. 1020.

condition of calcium in the blood rather than Paton's view that it is due to the toxic action of guanidines. This tendency will be greatly strengthened by the new work. Collip, Clark, and Scott [35, 36] extracted fresh ox-glands with 5% hydrochloric acid at 100° for 1 hour, and removed fat and the bulk of protein matter by simple means. Oral, subcutaneous, or intravenous administration of the extract prevented the onset of tetany in dogs from which the parathyroid glands had been removed, or cured the condition if it had appeared. The immediate effect of the administration was to cause a rise in the concentration of calcium in the blood, and the relief of tetany or its prevention was associated with this rise. The influence of the parathyroid extract on the level of blood calcium was most remarkable, for it was found possible by raising the dose of the active principle to bring about a condition of "hypercalcæmia," even to the extent of causing collapse and death when the normal concentration of calcium in the blood had been more than doubled.

The condition of "hypercalcæmia" is associated with a curious increase in the viscosity of the blood. Further experiments with a more carefully purified preparation of the hormone extracted from the glands indicated that whilst prolonged overdosage was invariably fatal, a single massive dose was relatively harmless.[37] The changes in concentration of calcium in the blood can be made the basis of a method of assay of the potency of the extracts.

It was found possible to produce tetany by injection of guanidine into dogs in which the calcium concentration of the blood had been raised by administration of the hormone; a result which seems clearly to dissociate guanidine tetany from that related to parathyroid deficiency, and to disprove the idea of an antagonism between the two agents. An improved method of preparation of the active principle has been described.[38] Preparations in 0·1*N*-hydrochloric acid retained their activity after keeping for 16 months in the ice-chest.

Thyroid.—Indirect light is shed on the nature of the active principle of the thyroid gland, thyroxin, by the interesting synthesis recently carried out by Harington.[39] It will be recalled that Kendall believed thyroxin to be a molecule containing the 4 : 5 : 6-tri-iodo-2 : 4 : 5 : 6-tetrahydroindole nucleus. The evidence in favour of this view was slender, and no answer has yet been

[35] *Nature*, 1925, **115**, 761.
[36] *J. Biol. Chem.*, 1925, **63**, 395, 439; *A.*, i, 754.
[37] Collip and Clark, *ibid.*, 1925, **64**, 485; *A.*, i, 1017.
[38] Hjort, Robison, and Tendick, *ibid.*, 1925, **65**, 117; *A.*, i, 1364.
[39] *Ibid.*, 1925, **64**, 29.

forthcoming to many calls for details of the synthesis of thyroxin which it was claimed had been effected by Kendall's colleague, Osterberg.[40] Harington considered that the properties of the substance described by Kendall would be more satisfactorily accounted for if the substance were a phenyl derivative of glutamic acid. Accordingly he attempted, and achieved, the difficult task of synthesising 3′ : 4′ : 5-tri-iodophenylpyrrolidonecarboxylic acid, a substance having practically the same empirical formula as that given for thyroxin by Kendall, which shows certain chemical similarities to the latter substance. The synthetic product was found to be without the effect on the basal metabolic rate which is characteristic of the thyroid principle.

The investigation of Hicks[41] on the ultra-violet absorption spectra of thyroxin and tryptophan indicate that an indole nucleus might be present in the former substance.

Kendall regards 2-hydroxyindole-3-β-propionic acid as the precursor of the active principle and has published his views on its *rôle* as a catalyst of intravital oxidations.[42]

Ovarian Hormone.—Since Adler[43] first succeeded in producing artificial œstrus in animals by the injection of aqueous extracts of whole ovaries, a number of methods for the preparation of active extracts have been described. Of these the most important seems to be that of Hermann and Frankel,[44] who protected their process by patent rights. The alcoholic extract of ovaries, after removal of the solvent, was treated with ether and acetone to remove certain lipoid constituents; the bulk of the cholesterol was then removed by fractional crystallisation. The active material could, it was stated, be further concentrated by distillation at 190° under low pressures.

General confirmation of many of the observations of Hermann and Frankel, which formerly received curiously little attention, has recently been provided by the work of Allen and Doisy[45, 46] and of Dickens, Dodds, and Wright.[47] The latter investigators have prepared a highly active material in the form of a clear, light brown oil, soluble in the chief fat-solvents. Its activity is unaffected by the removal of cholesterol or by heating to 200°, but seems to be lessened by treatment with alcoholic sodium hydroxide. By means of a series of injections an ovariectomised rat was kept in a

[40] *Ann. Reports*, 1919, 1920, 1923. [41] *J.*, 1925, **127**, 771.
[42] *Proc. Soc. Exp. Biol. Med.*, 1925, **22**, 307.
[43] *Arch. Gynäk*, 1912, **95**, 349. [44] Eng. Pats. 113, 3111 of 1915.
[45] *J. Amer. Med. Assoc.*, 1923, **81**, 819.
[46] Doisy, Ralls, Allen, and Johnston, *J. Biol. Chem.*, 1923, **59**, xliii; 1924, **61**, 711.
[47] *Biochem. J.*, 1925, **19**, 851.

state of continuous œstrus for a period of 14 days. The production of the hormone is believed to be localised in the ovarian follicle.[48]

Insulin and Carbohydrate Metabolism.

The rate of growth of the literature dealing with insulin and its action is truly alarming, and each year renders the task of selecting a few papers for review more formidable.

The chemical nature of the active component of commercial insulin preparations has been studied by Abel and Geiling,[49] who confirm the generally-accepted view that such materials are very complex mixtures. Neglecting inorganic constituents, the American investigators were able to separate the hormone from a number of crystalline amino-acids and a variety of protein-like fractions. In the course of these processes the rabbit unit was raised from 8 or 12 to more than 40. Some evidence was obtained that the physiological potency is related to a form of labile sulphur in the product, and the authors are inclined to believe that this is an integral part of the insulin molecule. Phosphorus is not present. Their results are of great interest, but the evidence for their views regarding the association between physiological potency and the presence of labile sulphur is somewhat inadequate.

Burn and Dale [50] have studied the localisation of the action of insulin by observations on the decapitated and eviscerated cat. Such a preparation, in which a supply of sugar was provided by steady infusion of dextrose, showed the typical fall of blood-sugar level on injection of the hormone. Since the skin took no part in this, it must be attributed to the heart, lungs, and particularly the muscles. Confirmation of the increase in carbon dioxide production following insulin administration noted by previous investigators was obtained, and the authors also agree that the amount of the extra carbon dioxide is not sufficient to account for the sugar that disappears.

Further evidence has been forthcoming to support the view that insulin plays a part in the synthesis of phosphoric esters of sugar prior to its degradation.[51] Brugsch and Horsters [52] think, however, that in addition to synthesis of hexosephosphates the formation of polysaccharides is effected by insulin. In another paper [53] these investigators give reasons for believing that the tissues of depancreatised animals contain a normal amount of hexosephos-

[48] Allen, *Amer. J. Anat.*, 1924, **34**, 133.

[49] *J. Pharmacol.*, 1925, **25**, 421; *A.*, i, 1512 (abstract of earlier and preliminary communication).

[50] *J. Physiol.*, 1924, **59**, 164.

[51] See *Ann. Reports*, 1924.

[52] *Biochem. Z.*, 1924, **151**, 203; *A.*, 1925, i, 208.

[53] *Ibid.*, 1925, **155**, 459; *A.*, i, 483.

phatase, but that the synthetic action of the enzyme which builds up the phosphoric ester is inhibited in the absence of insulin. Some evidence is also being obtained that insulin accelerates the breakdown of sugar by lower organisms. Noyes and Estill [54] find increased production of lactic acid from sugar by *Lactobacillus bulgaricus* and *L. acidophilus* when insulin is present.

Much uncertainty still prevails regarding the nature of the blood sugar, and the changes which, as some think, occur in its molecule under the action of insulin. Lundsgaard and Holbøll found that when glucose solution was incubated at body temperature with finely divided muscle tissue the optical rotatory power and reducing values agreed. If insulin was present, the former diminished.[55, 56] These results, as well as others they have recently reported,[57] confirm in many essentials the observations of Winter and Smith.[58] They could, however, be accounted for by a change in the equilibrium between α- and β-glucose, without assuming the formation of a hypothetical γ-glucose.

The new form of dextrose with low reducing power has been termed by them *neoglucose*. Winter and Smith,[59] continuing their study of the nature of the blood sugar, have found that the optical rotation of diabetic blood is considerably increased on mild hydrolysis, and that phenylosazones with crystalline forms differing from that of glucosazone can be prepared.

Whilst it is almost certain that obscure changes do occur in the blood sugar under certain conditions in the body, it is also apparent that small changes in the optical rotations of complex mixtures such as protein-free blood filtrates must be exceedingly difficult to interpret.

In this connexion Holden,[60] who has identified the reduced form of glutathione as a constituent of red blood corpuscles, believes that the presence of this optically active substance in the protein-free blood may be responsible for many of the effects noted by Winter and Smith and others, and offered by them as evidence of the presence of different forms of blood carbohydrate. Visscher [61] attributes their results to variations in the reactions of the blood filtrates.

The breakdown of carbohydrates in muscle remains the subject of considerable interest. Embden and Zimmermann [62] have now

[54] *Proc. Nat. Acad. Sci.*, 1924, **10**, 415; *A.*, 1925, i, 107.
[55] *Compt. rend. Soc. Biol.*, 1924, **91**, 1108.
[56] *J. Biol. Chem.*, 1924, **62**, 453; *A.*, 1925, i, 208.
[57] *Compt. rend. Soc. Biol.*, 1925, **92**, 387, 395, 398, 525.
[58] *Ann. Reports*, 1922, p. 195.
[59] *Proc. Roy. Soc.*, 1924, **97**, *B*, 20.
[60] *Biochem. J.*, 1925, **19**, 727.
[61] *Amer. J. Physiol.*, 1924, **68**, 135; *A.*, 1925, i, 1343.
[62] *Z. physiol. Chem.*, 1924, **141**, 225; *A.*, 1925, i, 729.

placed beyond question the identity of the hexose diphosphate (lactacidogen) of muscle with that originally isolated by Harden and Young from the fermentation of sugar by yeast. The two substances gave rise to the same neutral brucine salt.

Embden has somewhat disturbed the accepted views on acid production in muscle during contraction by his announcement that in the first phase, in which tension is developed, twentyfold as much phosphoric acid as lactic acid is produced.[63] After a short tetanus, lactic acid, but not phosphoric, continues to be produced for a few seconds, hence the liberation of energy due to the formation of lactic acid is not limited to the phase of shortening. The phosphoric acid liberated in the early stage of tetanus may disappear during the later stages, whilst lactic acid is still being formed. These observations suggested to Embden that the liberation of each of the two acids has its own special relation to the phenomena of contraction; it is possible that the sudden liberation of phosphoric acid produces a single contraction, whereas lactic acid alone is mainly responsible for producing maintained contractions.

Meyerhof, Lohmann, and Meier [64] have found that pyruvic acid was able to replace lactic acid in the resynthesis of glycogen in muscle, whereas dihydroxyacetone, glyceraldehyde, dihydroxymaleic acid, glycollaldehyde, and methylglyoxal were of no value in this respect. The parallel between the modes of breakdown of sugar by plant cells and by animal cells is also emphasised by the clear indications from the work of Neuberg and Gottschalk [65] that acetaldehyde is normally a step in the oxidation of sugar by muscle. The aldehyde was isolated by the "fixation" method with calcium sulphite, and appears to be formed by the action of decarboxylase on pyruvic acid. It has also been identified amongst the products of respiration of higher plants.[66]

Glutathione.

The outstanding paper of the year in the field of research on biological oxidations is one from the laboratory of Sir Gowland Hopkins on glutathione with reference to its influence on the oxidation of fats and proteins.[67] Before dealing with the contents of that paper in some detail, reference must be made to the success which has rewarded the efforts of Hopkins's colleagues, Stewart and Tunnicliffe, to synthesise the dipeptide.[68] Its constitution as a diglutamylcystine is now definitely established.

[63] *Klin. Woch.*, 1924, **3**, 1393.
[64] *Biochem. Z.*, 1925, **157**, 459; *A.*, i, 727.
[65] *Ibid.*, 1924, **151**, 169.
[66] *Ibid.*, 1925, **158**, 253; **160**, 256.
[67] *Biochem. J.*, 1925, **19**, 787; *A.*, i, 1499.
[68] *Ibid.*, p. 207; *A.*, i, 795.

It will be recalled that Hopkins and Dixon showed that washed muscle tissue that had been extracted with boiling water, washed with alcohol, dried in a vacuum and powdered was capable of taking up considerable quantities of oxygen in the presence of glutathione.[69] The oxygen uptake when Clarke and Lubs's phosphate buffer media were employed was of the order of 400 c.mm. per gram of dry powder. It has now been found that the high concentration of phosphate in the fluid exerted an inhibitive action, and that with preparations of the tissue component and glutathione in Ringer's fluid the oxygen uptake might be as much as five times as great. Even higher values, 5,000 c.mm. per gram, have been recorded by Meyerhof,[70] who used preparations of the thermostable muscle component and thioglycollic acid, but the conditions differed from those prevailing in Hopkins's studies. The further work both of Hopkins and of Meyerhof suggested that the substance in the dried, extracted tissue which formed with glutathione, or similar substance, an oxidation-reduction system might well be one containing unsaturated fatty acids in its molecule.[71] To this point Hopkins gives attention in his recent paper.

In acid solution, p_H 3·0—4·0, the reduced form of glutathione catalyses the oxidation of unsaturated fatty acids, probably, Hopkins thinks, by a mechanism such as Meyerhof [72] suggested :

$$\begin{matrix} G{-}SH \\ G{-}SH \end{matrix} + O_2 \rightarrow \begin{matrix} G{-}SH{-}O \\ G{-}SH{-}O \end{matrix} \xrightarrow{M} \begin{matrix} G{-}SH \\ G{-}SH \end{matrix} + MO_2.$$

When, however, the solution is nearly neutral, or its hydrogen-ion concentration is that of living animal tissues, the heterogeneous system presented by an aqueous emulsion of unsaturated fatty acids and reduced glutathione exhibits quite another behaviour. Under these conditions, the dipeptide is rapidly oxidised to the disulphide form, so that the system becomes inert before more than a small proportion of the fatty acid has been oxidised. In the presence of relatively high concentrations of glutathione, however, it is possible to determine that there is still a quantitative relation between the oxidation of the –SH group and that of the fatty acid, but it is not of the type that has been traced when the reacting system is definitely acid. In the neighbourhood of neutrality it would seem as if the reaction involving simultaneous oxidation of the peptide and fatty acid were more of the type :

$$\begin{matrix} G{-}SH \\ G{-}SH \end{matrix} + O_2 \rightarrow \begin{matrix} G{-}SH{-}O \\ G{-}SH{-}O \end{matrix} \xrightarrow{M} \begin{matrix} G{-}S \\ G{-}S \end{matrix} + MO + H_2O.$$

[69] *Ann. Reports*, 1922.
[70] *Pflug. Arch.*, 1923, **199**, 531; *A.*, 1924, i, 118.
[71] *Ann. Reports*, 1923. [72] *Pflug. Arch.*, 1923, **199**, 531; *A.*, 1924, i, 118.

Curiously enough, the glycerides exhibit a behaviour differing in certain respects from that of the free fatty acids or their sodium salts. Hopkins has as yet obtained no clear evidence upon which to base an explanation of the difference, but records the interesting fact that lecithin behaves like the latter rather than the former. Meyerhof believed that the oxygen uptake of thermostable preparations of washed muscle in the presence of the sulphydryl group became so small after further repeated extractions to remove all fatty substances that it was negligible. This Hopkins considers to be due to the hydrogen-ion concentration of the systems studied by the German investigator. Thus, at p_H 3·5 such a system exhibited no uptake at all, but at p_H 7·6 it absorbed oxygen to an extent never less than that of the preparation before extraction of the fatty constituents. It was found that the fully-extracted tissue possesses at p_H 7·6 the power to reduce the disulphide form of glutathione, and this, Hopkins discovered, is brought about by the action of protein. It is a curious fact that muscle tissue washed exhaustively to remove soluble constituents still gives a strong nitroprusside reaction, which Hopkins and Dixon attributed to a "fixed –SH group." Although no absolute proof has been given that the reaction is due to this group, almost all the observed facts can be explained on the assumption that it is. Furthermore, Hopkins has been at some trouble to satisfy himself that the so-called "fixed –SH group" is in reality a unit of the protein constituents of the tissue residue. His experiments with tissue preparations indicate that at p_H 7·6 the sulphydryl group of the proteins of the thermostable muscle residue is the only reducing agent left, and probably the only factor, even in muscle which has been simply washed, which reduces glutathione. Szent-Györgyi's assumption [73] that the fixed –SH is not oxidised by the disulphide glutathione is shown to be unjustified.

Conclusive evidence that the special characters of the fat-free muscle preparations are due to their proteins is provided by experiments on the oxygen uptake of pure proteins in the presence of glutathione. First, it will be recalled that Heffter [74] and Arnold [75] showed that whereas the proteins of blood plasma gave no nitroprusside reaction they could be made to yield the characteristic colour after treatment with sodium sulphite. Secondly, egg-albumin, which gives no reaction in its natural state, does so after it has been "denatured." These curious facts were further examined by Harris,[76] who concluded that they might be accounted for by

[73] *Biochem. Z.*, 1925, **157**, 50. [74] *Mediz. Naturwiss. Arch.*, 1907, **1**, 81.
[75] *Z. physiol. Chem.*, 1914, **70**, 300.
[76] *Proc. Roy. Soc.*, 1923, **94**, *B*, 426, 441.

assuming the existence in the molecule of a thiopeptide linking which on hydrolysis or keto-enol transformation would give rise to the –SH group. Hopkins has now shown that the reaction is due to the reduction of a group in the protein complex. No protein which fails to exhibit a nitroprusside reaction shows any tendency to reduce solutions of the disulphide, whilst a protein such as gelatin, devoid of sulphur, cannot be made to yield the nitroprusside reaction.

Glutathione, in promoting the oxidation of the reduced protein, *i.e.*, one giving the nitroprusside reaction for the –SH group, causes an oxygen uptake more or less proportional to the amount of sulphydryl group judged to be present, but it may be as much as ten times that which would be necessary to oxidise the group itself. On the cessation of oxygen uptake, which occurs when the nitroprusside reaction is no longer given, it is possible to reduce the protein once again by treatment with reduced glutathione or thioglycollic acid, and the newly reduced protein exhibits once again the capacity for oxygen uptake.

In this manner, it is possible alternately to oxidise and reduce protein so that the total oxygen uptake may be as high as 10 c.c. of oxygen per gram. It would seem, therefore, that within physiological ranges of reaction it is the proteins of the washed muscle tissues that are responsible for the reduction of glutathione. The process can scarcely be merely one of hydrogen transport, for, as has been stated above, the oxygen uptake may be tenfold that required for oxidation of the sulphydryl group in the protein. No evidence is yet available to account for this remarkably interesting fact.

A study of the influence of hydrogen-ion concentration on the system thermostable muscle preparation–glutathione clears up a number of differences between the results recorded by Meyerhof and by Hopkins. At p_H 3·0—4·0, fat alone is oxidised, whether the reduced or the oxidised form of the dipeptide be present. At p_H 6·0, both fat and protein are oxidised in each system, whereas at p_H 7·6 the oxidation of fat is almost completely suppressed and that of protein is predominant. Hopkins's concluding paragraph is worth quoting. "I am well aware indeed that on first acquaintance the curious and at many points obscure phenomena described in this paper may seem to lack biological reality. The experimental results . . . are yielded by systems which contain actual cell constituents in contact with one another, and depend upon actual properties of these constituents. Such studies would seem to be a necessary, if remote, antecedent to a fuller understanding of the behaviour of the same constituents in the organised phenomena of the living cell itself."

Oxidation of Fats.

The study of the oxidation of fats, to which the work of Hopkins, dealt with in the previous section, directs attention, has been considerably advanced by the investigations of Clutterbuck and Raper.[77] For a long time it has been taught that oxidation of the saturated fatty acid molecules in the living body occurs at the β-carbon atom, so that the carbon chain is progressively shortened by losing two atoms at a time. This theory was based to a large extent on the well-known researches of Knoop,[78] in which he studied the fate in the animal body of the phenyl derivatives of a series of fatty acids, and was strongly supported by the observations of Dakin [79] on the oxidation of the ammonium salts of the acids by hydrogen peroxide.

Clutterbuck and Raper, using conditions similar to but not identical with those of Dakin, obtained products which showed that oxidation could occur at the γ- and δ-carbon atoms, and possibly also at the α-. So far as could be determined in the case of stearic, palmitic and myristic acids, γ- and δ-oxidations seemed to take place to about the same extent.

In 1916 Hurtley [80] published a careful study of the 4-carbon-atom acids of diabetic urine in which he came to the conclusion that the theory of β-oxidative degradation of fatty acids in the animal body is inadequate. This view was supported by an experimental investigation of the oxidation of butyric acid by hydrogen peroxide in which he obtained over 50% of the theoretical yield of succinic acid.[81]

This fact is of particular interest, because Clutterbuck and Raper, although as yet uncertain as to the further stages in the oxidation of the γ- and δ-keto-acids yielded by oxidation of the fatty acids with hydrogen peroxide, find that both yield succinic acid. This means that the carbon chain breaks between the γ- and δ-carbon atoms to yield the 4-carbon acid.

Whether other forms of oxidation than that at the β-carbon atom occur in the living body is not yet known, but the authors remark on the probability that the fatty acids placed in an environment with a suitable oxidation potential will be oxidised in a manner dependent on the structure of the acid rather than on the means by which the necessary potential is obtained.

Another interesting point revealed by their experiments is that the first step in the oxidation of the saturated acids is probably

[77] *Biochem. J.*, 1925, **19**, 384.
[78] *Beitr. Chem. Physiol Path.*, 1904, **6**, 150.
[79] *J. Biol. Chem.*, 1908, **4**, 77, 221, 227, 419; *A.*, 1908, i, 74, 119; ii, 720.
[80] *Quart. J. Med.*, 1916, **9**, 301.
[81] Cahen and Hurtley, *Biochem. J.*, 1917, **11**, 164.

the production of a series of keto-acids and not hydroxy-acids. This is quite in accordance with the opinion expressed in 1916 by Hurtley, and is also in agreement with the recent observations of Quastel, to which reference is made on p. 231. The formation of succinic acid as an intermediate product of the metabolism of fatty acids *in vitro* and the probability that it also occurs *in vivo* greatly emphasise the importance of the thermolabile system (succinoxydone) which Batelli and Stern discovered in muscle.[82] The former even suggests a possible path by which fatty acids might give rise to sugar, for succinic acid is known to be easily converted into fumaric and malic acids in the tissues, and the latter is converted into glucose in the animal exhibiting phloridzin diabetes.

Bacterial Metabolism and Anaërobiosis.

During the past year or two, considerable attention has been devoted, particularly by the Cambridge school of biochemistry, to chemical changes brought about by bacterial action.

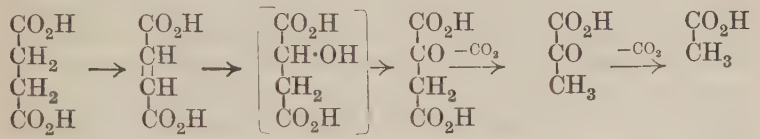
Stephenson and Whetham [83] noted that in its early stages the degradation of glucose by *Bacillus coli* is almost anaërobic in character. Increasing the tension of oxygen resulted in an increase in the absorption of the gas and also in the output of carbon dioxide, without a parallel rise in the utilisation of sugar occurring. At the same time, the inhibition of bacterial activity due to the accumulation of acidic products was definitely retarded. It was concluded that the increased oxygen uptake indicated the breakdown of some of the inhibiting acid metabolites. The breakdown of glucose under anaërobic conditions is readily effected by *B. coli*, but no oxidation of lactic, succinic, or acetic acid or glycerol occurs. The reason for this is at once apparent from a consideration of the energetics of the reactions, for whereas the breakdown of glucose to lactic acid liberates a supply of energy for utilisation by the bacteria, as far as can be determined, all the likely paths of anaërobic metabolism of the other substances would be endothermic reactions.

This view is supported by the observation that *B. coli* possesses a thermolabile system (enzyme) capable of catalysing the reduction of methylene-blue in the presence of succinates under anaërobic conditions, and by the fact that this organism grows anaërobically with pyruvic, lactic, succinic, or fumaric acid or glycerol as the sole source of carbon, provided nitrates are present to act as a hydrogen acceptor enabling oxidations to proceed along the path normally followed under aërobic conditions.[84] The actual steps by which the sugar molecule is degraded are becoming clearer. After the

[82] *Biochem. Z.*, 1911, **30**, 172. [83] *Biochem. J.*, 1924, **18**, 498.
[84] Quastel and Whetham, *ibid.*, 1925, **18**, 519.

appearance of lactic acid, the formation of pyruvic acid has been observed.[85] This is, it is believed, broken down to acetaldehyde, then to acetic acid and alcohol.[86] The production of acetaldehyde during the fermentation of a large number of sugars and polyhydric alcohols by *B. coli* has been proved by employing the "side-tracking" reaction with sodium sulphite by which Neuberg demonstrated its formation during alcoholic fermentation by yeast.[87]

Some light is thrown on the intermediate metabolism of the carbon chain of aliphatic acids by studies on the action of bacteria on succinic and fumaric acids.[88] Both acids are fermented by *B. pyocyaneus* with the production of lower fatty acids, chiefly acetic; the fermentation being greatly accelerated by aeration. Measurements of the gaseous exchange satisfy the changes represented thus:



Some doubt exists, however, regarding malic acid as an intermediate product, because it is apparently unable to act as a hydrogen donator to methylene-blue under anaërobic conditions.[89] This seems to suggest that oxalacetic acid may be derived directly from fumaric, which, if true, is not in accordance with Wieland's theory of dehydrogenation. Fumaric acid has been detected amongst the products of fermentation of malic acid, but no trace of malic acid was found in the fermentation of fumaric acid.[90]

Further examination of the dehydrogenations produced by bacteria show that anaërobic growth can be correlated with the activating powers of the organisms. Growth under anaërobic conditions is only possible when the bacteria possess a system capable of activating some constituent of the medium to act as a hydrogen acceptor.[91, 92, 93]

The widespread employment of methylene-blue as a reduction indicator in biological studies such as these has led Clark, Cohen, and Gibbs [94] to investigate the equilibrium values of the reversible

[85] Quastel, Stephenson, and Whetham, *Biochem. J.*, 1925, **19**, 304.
[86] Aubel and Salabarton, *Compt. rend.*, 1925, **180**, 1183.
[87] de Graaff and le Fevre, *Biochem. Z.*, 1925, **155**, 313.
[88] Quastel, *Biochem. J.*, 1924, **18**, 363.
[89] Quastel and Whetham, *ibid.*, p. 519.
[90] Emmerling and Reiser, *Ber.*, 1902, **35**, 700.
[91] Quastel, *Biochem. J.*, 1924, **18**, 365.
[92] Quastel and Wooldridge, *ibid.*, **19**, 652.
[93] Quastel and Stephenson, *ibid.*, 660. [94] *J. Biol. Chem.*, 1925, **63**, liv.

change. It has been established that the two electrochemical equivalents concerned in the oxidation–reduction process are associated with exactly the same energy intensity, and that the hydrogen atoms entering into the ordinary formalistic equation of reduction are associated with ionisation constants of enormous differences. This might be inconsistent with a mechanical interpretation of Wieland's theory. It is inferred that the reduction of methylene-blue consists in the transfer of an electron pair to this oxidant, with or without the subsequent addition of one or the other of the components of water according to the acid-base equilibrium of the solution.

Electrode potential measurements with suspensions of bacteria gave data agreeing with those calculated from the data for the reduction of methylene-blue. The potentials thus established by two methods lie in a zone where there can be no appreciable quantity of either molecular hydrogen or molecular oxygen in equilibrium with the system. If either gas be present, it can be considered in relation to a dynamic process only, and not to a static equilibrium. In this connexion, Thunberg [95] has recently studied the reduction–oxidation potential of the succinic acid–fumaric acid system containing succino-dehydrogenase, using the values for the oxidation–reduction potential of mixtures of methylene-blue and leuco-methylene-blue determined by Clark at different hydrogen-ion concentrations.

Another aspect of anaërobic growth of bacteria concerns the limited tolerance of oxygen exhibited by the organisms which normally flourish in the absence of air. Callow [96] has pointed out that Wieland's theory of cell respiration holds that water is split into (HO) and (H), the latter combining with the oxygen of the air to form hydrogen peroxide, which is immediately broken down by the widely distributed enzyme catalase with production of atomic oxygen. If an organism lacked the power to decompose hydrogen peroxide, the accumulation of this substance would readily account for the inhibitory action which atmospheric oxygen has on anaërobes. Of nine anaërobic organisms studied, none was found to contain catalase, whilst twelve aërobic species were capable of decomposing hydrogen peroxide.

Callow failed to demonstrate the presence of hydrogen peroxide in cultures of anaërobic organisms, but M'Leod and Gordon, whose conclusions in general coincide with those of Callow, were able to do so.[97]

Of some bearing on the oxidation–reduction systems of bacteria

[95] *Skan. Arch. Physiol.*, 1925, **46**, 339.
[96] *J. Path. Bact.*, 1923, **26**, 320.
[97] *Ibid.*, p. 33.

is the question whether they contain glutathione. M'Leod and Gordon, who obtained positive colour tests, think the reactions were due to the reduction by the organisms of oxidised dipeptide in the broth.[98] Callow and Robinson, on the other hand, are inclined to believe that certain bacteria actually form a substance giving the nitroprusside reaction. It is uncertain whether this substance is glutathione or not. It is not hydrogen sulphide.[99]

Some years ago Weinland [1] reported that the intestinal worm, *Ascaris lumbricoides*, does not require oxygen for its metabolism and lives equally well in atmospheres of inert gases. To account for the ability to perform muscular movements under these conditions Weinland suggested that the energy is derived from the breakdown of glycogen according to the equation

$$4C_6H_{10}O_5 + 4H_2O = 9CO_2 + 3C_4H_9{\cdot}CO_2H + 9H_2.$$

He detected carbon dioxide and a volatile acid resembling valeric acid, but was forced to assume that the hydrogen is taken up by a hydrogen-acceptor and is not liberated. Weinland satisfied himself that the valeric acid was not produced by contamination with bacteria, but Fischer [2] has recently demonstrated that he was incorrect and that the only acids formed under conditions of sterility are lactic and phosphoric acids. Slater [3] has submitted Weinland's work to a careful re-examination, and has found that although the worms are capable of prolonged existence in the absence of air, they achieve this only by restricting their movements. For their metabolism they undoubtedly require oxygen or its equivalent. Confirmation of the view that the volatile acids are products of bacterial contamination was also obtained by him.

Enzyme Action.

For a number of years past, the output of literature dealing with enzyme action has been very large, but in the opinion of the reporter the proportion of papers that have announced results of any outstanding interest has been curiously small.

Dealing with general principles, the paper by Briggs and Haldane,[4] in which an examination is made of the theoretical basis of the equation of Michaelis and Menten,[5] applied with success by Kuhn and others to numerous cases of enzyme action,[6] is a valuable contribution.

The same may be said of a series of papers from the Toronto

[98] *Biochem. J.*, 1924, **18**, 937.
[99] *Ibid.*, 1925, **19**, 19.
[1] *Z. Biol.*, 1901, **42**, 55; 1902, **43**, 86.
[2] *Biochem. Z.*, 1924, **144**, 224.
[3] *Biochem. J.*, 1925, **19**, 604.
[4] *Ibid.*, p. 338.
[5] *Biochem. Z.*, 1913, **49**, 333.
[6] Oppenheimer's "Die Fermente und ihre Wirkungen," 1924, 185.

school of biochemistry, in which are described researches on the enzymic synthesis of proteins. As far back as 1886 Danileffsky observed the formation of a precipitate (plastein) when stomach extract was added to a concentrated solution of the products of peptic hydrolysis, and drew the conclusion that synthesis of a substance resembling a native protein had occurred. General confirmation of this observation was provided by Sawjaloff and other workers,[7] but the conditions under which synthesis occurs had not been at all clearly defined. Hesse [8] obtained plastein formation from Witte's peptone by papain or rennet at p_H 2·8 to 5·4, but not when the acidity was greater than p_H 2·8. No synthesis took place when the enzymes were inactivated. Wasteneys and Borsook [9] have recently found that by the action of pepsin at p_H 4·0 on a concentrated solution of the products of peptic hydrolysis of egg-albumin a precipitate is formed which contains as much as 39% of the nitrogen of the original solution, and is of the order of molecular complexity of the original protein. Plastein is rapidly hydrolysed by pepsin at p_H 1·7, but the proteoses left in solution after plastein has been synthesised are not attacked by the enzyme. This points to the re-formation by pepsin of a particular linking which under other conditions of dilution and acidity may be ruptured by hydrolysis. The effect of concentration is, as the earlier work indicated, marked. Between concentrations of substrate (hydrolysed products) corresponding with about 8% and 25% of protein, the amount of protein synthesised by pepsin at the optimum hydrion concentration, p_H 4·0, increases directly with the concentration. Below 8% no synthesis takes place, and it is inhibited above 25%. Peptic hydrolysis of egg-albumin can proceed to completion only when the concentration of protein is 6% or less. The interesting observation is recorded that by the action of trypsin at p_H 5·7 on a solution of the products of peptic hydrolysis of egg-albumin a substance was obtained having similar properties to the protein synthesised in the experiments with pepsin.

Considerable light has been thrown upon the mechanism of the action of tyrosinase on tyrosine by a series of careful investigations made in the past few years in Professor Raper's laboratory at Manchester. In 1923 it was shown that the formation of melanin takes place in stages, which can be clearly distinguished. Of these the first appears to be an oxidative one whereby the tyrosine is converted by the enzyme into a red pigment which is the first

[7] *Z. physiol. Chem.*, 1907–8, **54**, 119; *A.*, 1908, i, 234.

[8] *Arch. Verdauungskr.*, 1923, **31**, 275.

[9] *J. Biol. Chem.*, 1924, **62**, 15; 1925, **62**, 633, 675; 1925, **63**, 563, 575; *A.*, i, 102, 472, 865.

visible sign of oxidation. At p_H 6·0 this product is the main pigmented substance formed, but in less acid solutions it rapidly passes into a colourless substance and finally into melanin.[10] Of these last two changes the former appears to be of the nature of an intramolecular rearrangement, whilst the latter is an oxidation greatly accelerated by the phenolase present in the preparations of tyrosinase.

In the past, almost all theories of the action of tyrosinase on tyrosine were based on the assumption that deamination of the amino-acid takes place in the first phase. Thus Bach,[11] who was largely responsible for this view, suggested that the action of tyrosinase on tyrosine was to convert it into hydroxyphenylacetaldehyde, ammonia, and carbon dioxide, with the intermediate formation of the corresponding keto-acid. Later, in his opinion, came a complex change in which oxidation of the aldehyde, before or after condensation with ammonia, led to the formation of melanin. This view was accepted by Onslow.[12] The studies of Raper and Wormall[13] show, however, that there are no grounds for the assumption that deamination occurs, for not only is there no production of ammonia during the oxidation of tyrosine by tyrosinase, but the enzyme has no action on solutions of *p*-hydroxyphenylpyruvic acid, either in the presence or absence of ammonia.

Happold and Raper[14] support this evidence with the observation that there is no aldehyde formation, liberation of ammonia or decrease in amino-nitrogen when tyrosinase (potato) acts on glycine, alanine or phenylglycine. The formation of ammonia noted by Chodat and Schweizer[15] when tyrosinase acted upon amino-acids was due to the *p*-cresol that was added as a component of the reacting system. The same action is shown by phenol and catechol, but not by resorcinol, quinol or *p*-benzoquinone. Much the same conclusions were reached by Robinson and McCance.[16] It is suggested by Happold and Raper that certain phenols in the presence of amino-acids form intermediate *o*-quinone derivatives which attack the amino-acids with liberation of ammonia. The necessity of an amino-group for melanin formation is also apparent from the studies of Gortner,[17] who found that whereas both tyrosine and *p*-hydroxyphenylethyl alcohol are oxidised by tyrosinase to a

[10] *Biochem. J.*, 1923, **17**, 454.
[11] *Biochem. Z.*, 1914, **60**, 221; *A.*, 1914, i, 445.
[12] *Biochem. J.*, 1923, **17**, 216.
[13] *Ibid.*, 1925, **19**, 84; *A.*, i, 473.
[14] *Ibid.*, p. 92; *A.*, i, 474.
[15] *Arch. Sci. Phys. Nat.*, 1913, **35**, 140.
[16] *Biochem. J.*, 1925, **19**, 251.
[17] *Proc. Soc. Exp. Biol. Med.*, 1924, **21**, 543: *A.*, 1925, i, 474.

red pigment, only in the former case does the oxidation proceed to the formation of black pigments.

These new observations on the action of tyrosinase are closely related to those recorded by Onslow and Robinson,[18] who find that an enzyme preparation from the potato tuber oxidises tyrosol, *p*-cresol or phenol to dihydroxy-derivatives which give rise to peroxides.

3 : 4-Dihydroxyphenylalanine, for some time past regarded as a probable early stage in the oxidation of tyrosine *in vivo*, is oxidised by the potato enzyme to a red pigment, which in turn becomes a black melanin. Onslow and Robinson think that the 3 : 4-dihydroxyphenylalanine suffers oxidative deamination with formation of 3 : 4-dihydroxyphenylacetaldehyde and ammonia, which later take part in the formation of melanin. As we have seen, the work of Raper and his colleagues throws doubt on this theory.

Plant and Animal Nucleic Acids.

Observations that may seriously disturb accepted views regarding the relation between the nucleic acids from plant and from animal sources are reported from the laboratory of Walter Jones.

It will be recalled that the former acids were considered to be clearly differentiated from the latter by their containing uracil instead of thymine as one of the two pyrimidine bases in the molecule, and a pentose instead of a hexose sugar. It has, however, long been known that two substances, inosinic acid and guanylic acid, closely related in structure to the units of plant nucleic acids, can be isolated from animal tissue. Formerly it was somewhat generally assumed that they were derived from plant foods eaten by the animal; an explanation that had always seemed unconvincing. In 1923, Jackson[19] demonstrated the presence of an adenine nucleotide in blood, and Jones and Perkins[20] have now reported that the β-nucleoprotein of the pancreas yields not only guanine nucleotide, but also adenine and cytosine nucleotides, in spite of the assumption made by certain experimenters that no adenine is present. The crystalline form, chemical composition, and properties of the isolated nucleotides correspond with those isolated from yeast nucleic acid. In a more recent paper,[21] it is shown that by treating yeast nucleic acid with dilute sodium hydroxide at room temperature it was decomposed into its constituent nucleotides without the separation of phosphoric acid or free purine bases, and without deamination occurring. The nucleo-

[18] *Biochem. J.*, 1925, **19**, 420.
[19] *J. Biol. Chem.*, 1923, **57**, 121; 1924, **59**, 529.
[20] *Ibid.*, 1924, **62**, 291.
[21] *Ibid.*, p. 557.

tides of guanine, adenine, and cytosine were isolated in quantity, but no trace of the corresponding uracil compound was detected; a fact all the more remarkable because of the ease with which this particular nucleotide can usually be separated. The conclusion is drawn, therefore, that the uracil derivatives hitherto described as isolated from yeast nucleic acid are secondary products arising from the corresponding cytosine derivatives. It seems probable, as Jones and Perkins remark, that the distinction between animal and plant nucleic acids will in future not be so definitely drawn.

Regarding the alternative structures proposed for the nucleic acids, Levene and Simms [22] have pointed out that the different theories require a different number of ionisable hydrogen atoms in the nucleotide molecule. The results of a study by electrometric methods of the dissociation constants of four nucleosides and the corresponding nucleotides are in harmony with the structure proposed by Levene [23] in so far as they indicate that the latter compounds possess only one (secondary phosphoric acid) group, which is dissociated at about p_H 6·0, whereas the theory of Jones [24] requires two ionisable hydrogen atoms in this region. Additional evidence in support of Levene's views of the structure of these compounds is provided by the examination of the nucleosides which he has synthesised.[25]

Hæmoglobin and Related Pigments.

A most important series of contributions to our knowledge of hæmoglobin has appeared from Professor Barcroft's laboratory. It has been found [26] that the blood pigment can exist as such only in the neighbourhood of neutrality, for in definitely acid or alkaline solutions it is converted into hæmochromogen. The formation of this substance does not, as was previously believed, involve the separation of globin from the iron-containing unit. Both hæmochromogen and its oxide, hæmatin, are conjugated proteins containing globin. Anson and Mirsky propose the name *hæm* for the non-protein part of the molecule containing pyrrole nuclei and iron.

Hæm may be prepared from hæmin by reduction by sodium hydrosulphite in alkaline solution, and it shows optical and chemical properties differing widely from those of hæmochromogen. It may, however, be converted into a substance indistinguishable from hæmochromogen by the addition of globin. Moreover, hæm may be combined with other proteins, amino-acid or nitrogenous

[22] *J. Biol. Chem.*, 1925, **65**, 519; *A.*, i, 1478.
[23] *Ibid.*, 1919, **40**, 415; *A.*, 1920, i, 193.
[24] *Amer. J. Physiol.*, 1920, **52**, 193; *A.*, 1920, i, 687.
[25] *J. Biol. Chem.*, 1925, **65**, 463; *A.*, i, 1463.
[26] Anson and Mirsky, *J. Physiol.*, 1925, **60**, 50; *A.*, i, 1475.

bases of various types to yield a variety of "hæmochromogens," all of which have similar but not identical properties. The importance of this discovery is far-reaching. In the first place it reveals the remarkable fact that hæm is the iron- and pyrrole-containing unit of probably all the natural pigments of the hæmoglobin type.[27] Keilin's studies[28] of the widely occurring respiratory pigment cytochrome (formerly known as myohæmatin or histohæmatin) support this view. The apparent universal presence of hæm as a constituent part of the respiratory pigments of plant and animal tissues renders unnecessary the assumption, in order to explain the haphazard distribution of hæmoglobin in nature, that the capacity to synthesise the iron-containing unit has been developed independently many times. In last year's Report attention was directed to the indications from Barcroft's work that the nature of the protein bound to the iron-containing unit appeared profoundly to affect the gas-binding powers of the pigment. The new researches on hæm go some way towards making clear how this occurs. Hæm itself is from the biological standpoint an impossible gas carrier, if for no other reason than because it is practically insoluble in water. A study of the influence of globin on the properties of hæmoglobin has been made by comparing hæm, a series of hæmochromogens and hæmoglobins in respect to their combination with carbon monoxide under different conditions. This study supports the conception of the blood pigment as a most highly evolved substance. α-Hæmochromogen, β-hæmochromogen, and hæmoglobin represent successive advances in the production from hæm of an ideal respiratory pigment. Space will not permit more than brief reference to an extremely valuable series of papers from the pen of Adair,[29] dealing with the physical chemistry of the hæmoglobin system. Also of importance are the observations of Conant and Fieser[30] on methæmoglobin. The nature of this curious compound at last seems reasonably clear. It appears that in the change from methæmoglobin to hæmoglobin one hydrogen atom is involved, and that the two pigments are related one to the other as are ferric and ferrous compounds.

Spermine.

Careful investigations of the occurrence and nature of this very interesting substance have recently been recorded. Rosenheim has made a valuable survey of the literature on spermine[31] and has

[27] Anson and Mirsky, *J. Physiol.*, 1925, **60**, 161; *A.*, i, 1476.
[28] *Proc. Roy. Soc.*, 1925, **98**, *B*, 312; *A.*, i, 1112.
[29] *J. Biol. Chem.*, 1925, **63**, 493, 499, 515, 517, 529; *A.*, i, 850, 851.
[30] *Ibid.*, 1925, **62**, 595; *A.*, i, 455.
[31] *Biochem. J.*, 1924, **18**, 1253; *A.*, 1925, i, 180.

explained many of the conflicting opinions and statements that have appeared. The characteristic crystals of the phosphate from semen were noted for the first time, not by Böttcher in 1865 as has generally been believed, but by Leeuwenhoek as far back as 1678. Several new methods for the preparation of the phosphate were worked out by Rosenheim, which led to its detection in various animal organs other than testes and in yeast.

Wrede and Banik [32] reinvestigated the base isolated from human sperm by Kunz,[33] who gave it the formula C_2H_5N. It was found to be cadaverine and not the base described as spermine by Schreiner in 1879.[34] The latter substance was prepared from human semen, and found to be represented by the formula $C_{10}H_{26}N_4$; its properties and salts were examined.[35] A fuller description of the isolation of spermine from tissues and of its chief salts is given in a paper by Dudley, M. C. Rosenheim, and O. Rosenheim,[36] who also adopt the formula $C_{10}H_{26}N_4$. It now appears highly improbable that this curious substance is in any way related to the internal secretion of the male reproductive organs, as was at one time imagined, and the elucidation of its constitution will be awaited with great interest.

J. C. Drummond.
H. J. Page.

[32] *Z. physiol. Chem.*, 1923, **131**, 29, 38.
[33] *A.*, 1888, 1122. [34] *A.*, 1879, 72.
[35] *Z. physiol. Chem.*, 1924, **138**, 119.
[36] *Biochem. J.*, 1924, **18**, 1263; *A.*, 1925, i, 294.

CRYSTALLOGRAPHY.

The death in 1919 of Professor E. von Fedorov from starvation as a consequence of the Russian revolution robbed the scientific world of one of the most brilliant crystallographers of all time. He it was who first proved the possibility of 230 types of crystal structure—a gigantic achievement in itself, although only one of many contributions to crystallography put forward by this remarkable man. Unfortunately, many of Fedorov's most interesting papers have remained entirely or too long in the original Russian, with the result that during his lifetime the author never received full credit for his work nor crystallography the full benefit of it. A life of struggle against many reverses and misunderstandings ended in tragedy. The pleasure was denied him of outliving the publication of what may be said to be his greatest conception, the practical expression of all his crystallographic ideas, "Das Krystallreich." * The preparation for publication of this enormous work was completed by his pupils in 1920, but it is only during the last twelve months that a copy has come into our hands.

The object of "Das Krystallreich" is the classification of all measured crystalline substances in a consistent and unambiguous manner so that the list may afford a rapid and trustworthy means of "crystallochemical analysis." From mathematical considerations of the space-lattices, Fedorov divides all crystals into two basic types, *cubic* and *hexagonal-prismatic*, the former in its turn being sub-divided into the *hexahedral*, *octahedral*, and *dodecahedral* classes, corresponding to the simple, body-centred, and face-centred cells, respectively. Furthermore, crystals of cubic type must be considered as either *tetragonaloidal* (the angle of the main prism lying between 45° and 52½°), or *trigonaloidal* (52½—60°). The hexagonal-prismatic type includes all hexagonal and hexagonaloidal crystals. Fedorov then supposes that the faces with the densest distribution of corresponding points are revealed by the characteristic habit of a crystal, *i.e.*, they predominate in a statistical investigation by reason of their large size and frequent occurrence. Such faces he denotes by the simplest indices and the other (less important) faces by more complicated ones. In accordance with this way of regarding the

* "Das Krystallreich. Tabellen zur Krystallochemischen Analyse." By E. von Fedorov. Pp. lxxiv. + 1050 + Atlas. VIII Series, Vol. xxxvi of the Proceedings of the Academy of Science of Russia.

morphology of crystals, the reader will find that for the majority of crystals described in "Das Krystallreich" the crystal-axes are different from those usually adopted (in Groth's "Chemische Krystallographie," for instance). Fedorov considered that for every crystal there is a "correct setting" ("die richtige Aufstellung"), which can be chosen from a study of the habit with the aid of certain rules enunciated by him. The characteristics of the habit are given by the "habit symbol" ("das Komplexsymbol"), in the general case

$$\begin{matrix} Ns; \pm\chi; \beta \\ \alpha \qquad \pm\psi . \\ \pm\phi \end{matrix}$$

In this symbol, $N = 3$, 4, or 6, according as the crystal is tri-, tetra-, or hexa-gonaloidal; s denotes the class of structure (h for hexahedral, o for octahedral, and d for dodecahedral; no letter is used for the prismatic class); α is the angle between the parametral plane and the basal pinakoid; ϕ is the deviation of the prism angle from the true tetragonal, trigonal, or hexagonal angle. The angles χ, β, and ψ express in a similar manner the deviations of monoclinic and triclinic crystals from ideal orthogonal cells.

After the "habit-symbol" of a substance has been derived according to the rules given by Fedorov, it is an easy matter to locate it in the tables. Accompanying it will be found a short description of the substance and the literature relating to it. In the case of symbols which are nearly the same, *e.g.*, those of isomorphous substances, the author recommends that advantage should be taken of the colour, melting point, and the simpler chemical reactions. In the introduction to the tables examples of the determination of the various types of structure are discussed and a short history of the question is given. The second volume of the work (which describes and classifies some 9000 crystals) is an atlas of stereographic projections of the crystals described in the first volume. Perhaps the most important feature of the work is the classification of crystals, not according to the ordinary crystal-class, but according to their basic structures as defined above. By this means Fedorov has succeeded in bringing out and emphasising very many interesting relations and resemblances between substances which were hitherto considered as unconnected. From the point of view of chemical crystallography, such an arrangement is invaluable. It is to be hoped that X-ray analysts will take immediate advantage of it.

The Structure of Quartz.

Of all the innumerable types of crystals which go to make up the earth's crust, probably quartz is the most celebrated. For hundreds

of years it has excited the interest and curiosity of the layman and professed scientist alike. It will be recalled that it was on quartz that Steno in 1669 established the Law of Constancy of Angle, that quartz was quoted by Haüy as a particularly good example of his principle of "hemihedrism," that in quartz Arago in 1811 discovered the phenomenon of optical activity and Biot the law connecting this activity with wave-length; and that through quartz also it was first pointed out by Sir John Herschel in 1822 that crystals which are dextrorotatory are mirror-images of crystals which are lævorotatory. Time and again attempts have been made on the problem of its structure, but with incomplete success even with the powerful resources of *X*-ray analysis. Although it was one of the earliest crystals to be examined by the new methods, it has been very difficult to draw any really satisfactory conclusions about the details of its structure. Recently [1] the problem has been attacked along new lines, with results which would appear to be very near the truth, since they afford a reasonable explanation of both the intensities of reflexion and the physical properties of the crystal, in particular the well-known series of twins.

At 575°, ordinary (α-) quartz changes to β-quartz, the transformation corresponding to a symmetry change from trigonal–trapezohedral, space-group D_3^4, to hexagonal–trapezohedral, space-group D_6^4. The latter form, being much the simpler structure of the two, is more amenable to *X*-ray analysis and has yielded data the interpretation of which has proved distinctly gratifying, not simply on its own account, but because of the direct indications which it gives of the structure of common (low-temperature) quartz. For all experiments point to this inference, *that α-quartz is a slightly distorted form of β-quartz*. The general features of the two lattices are remarkably alike. Disregarding the heat expansion, there is little to choose between them except with regard to the intensities of reflexion of the different planes, and these intensity variations, of course, contain the key to the problem of the actual distortion required to produce one form from the other. The solution of this question also has been attempted,[2] again with satisfactory agreement. A good idea of the structures now proposed for α- and β-quartz may be obtained from Figs. 1 and 2. The larger circles represent silicon atoms, the smaller ones oxygen. It will be easily seen how one structure is derived from the other. They are both built on the basis of a threefold spiral of silicon atoms with an approximate tetrahedral arrangement of oxygen atoms around each silicon atom. In the hexagonal form, this oxygen arrangement is

[1] W. H. Bragg and R. E. Gibbs, *Proc. Roy. Soc.*, 1925, *A*, **109**, 405.
[2] R. E. Gibbs, *ibid.*, 1925, *A*, **107**, 561; 1926, *A*, Feb.

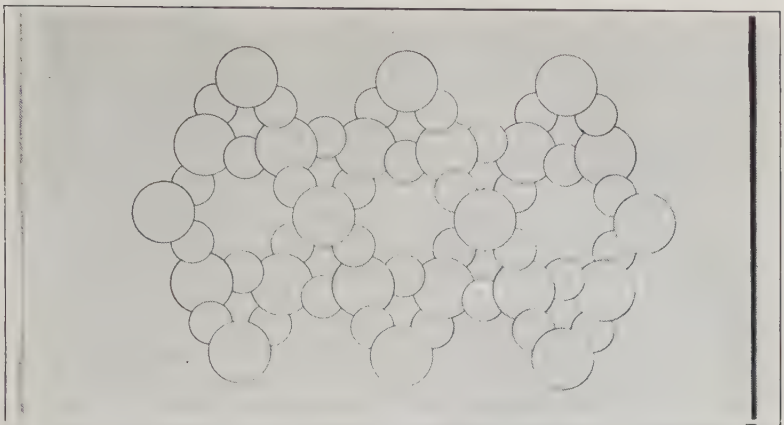


FIG. 1.

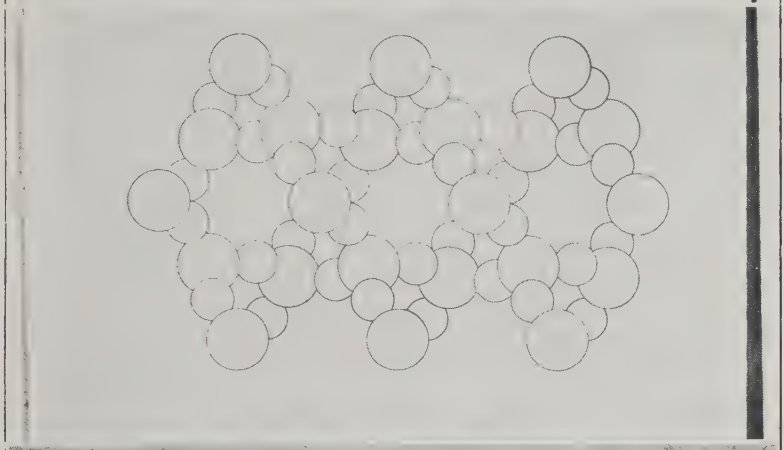


FIG. 2.

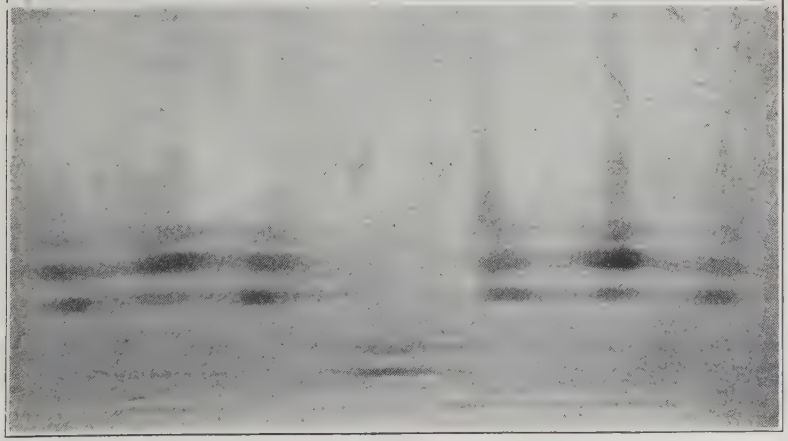


FIG. 3.

[*To face page* 242.]

almost exactly tetrahedral, and it is possible that it corresponds to a striving after the true tetrahedral symmetry which one might expect for the quadrivalent silicon atoms. It will be remembered that silicon itself crystallises after the manner of diamond, *i.e.*, each atom is tetrahedrally surrounded by four others, whilst the recently determined structure of β-cristobalite [2] (stable modification between 1470° and 1710° examined between 290° and 430°) preserves also the diamond arrangement of silicon atoms with an oxygen atom inserted between each pair. Thus in β-cristobalite each silicon atom is surrounded tetrahedrally by four oxygen atoms at distances of 1·541 Å.U., with each oxygen exactly halfway between two silicons, but in β-quartz each silicon is surrounded by oxygen atoms nearly tetrahedrally at distances of 1·55 Å.U. with the two oxygen–silicon linkings $\left(O\diagdown_{Si}\diagup O\right)$ *not* collinear but inclined at about 155°. In common (α-) quartz, it has been estimated [2] that the two oxygen atoms lie neither in the same planes as the silicon atoms nor half-way between them, but rather in planes about $c/9$ above and below the silicon planes. The regular tetrahedral character is lost, the oxygen–silicon linkings being now at about 147° due to a movement of the silicon atoms of about 0·3 Å.U. from their β-positions.

The structure of the two forms of quartz outlined above offers a very reasonable explanation of the remarkable twinning exhibited by α-quartz. The four well-known twins are all deduced in the original paper, to which reference should be made for details. The nature of other physical properties is also touched upon. A paper on β-quartz, giving similar experimental results and conclusions, is promised by Wyckoff.[4]

The Crystallography of Cellulose and Related Substances.

It is now five years since the problem of the structure of cellulose was first attacked by *X*-ray methods. Since then, thanks to the valuable work of the Kaiser Wilhelm Institut für Faserstoffchemie, an interesting series of experimental results has been recorded which, although a final solution is still not available, purely chemical investigators cannot afford to neglect. If only for this reason, a short review of the present situation seems desirable.

For cellulose itself, the crystallo-chemical conclusions remain substantially the same as they were in 1921.[5] The unit cell is orthorhombic or slightly monoclinic and contains the substance of

[3] R. W. G. Wyckoff, *Amer. J. Sci.*, 1925, **9**, 448.

[4] *Science*, 1925, **62**, 496.

[5] R. O. Herzog and W. Jancke, *Z. Physik*, 1920, **3**, 169; R. O. H., W. J., and M. Pólányi, *ibid.*, p. 343; M. Pólányi, *Naturwiss.*, 1921, **9**, 288; R. O. Herzog, *Cellulosechem.*, 1921, **2**, 101; 1925, **6**, 39; *A.*, i, 639.

four $C_6H_{10}O_5$-groups. The cell-edge which generally lies parallel to the fibre-axis seems to be fairly accurately determined and is the same for the many varieties of cellulose that have been tested. The lengths of the other two edges cannot be considered so trustworthy, for it is impossible to take rotation photographs about them, but it is very probable that the smallest group which is regularly repeated throughout the structure is $(C_6H_{10}O_5)_4$. This group may conceivably have to be multiplied by two, four, eight, or even a higher number (although the evidence is as yet rather against such multiplication), but odd multiples, such as three or five, of $(C_6H_{10}O_5)$ are excluded. Attempts have been made to enunciate something chemically more definite than this, but the discussion of these may be left to the expert in cellulose chemistry. In any case, there is still much more crystallographic information required before we can feel we are on safe ground. Most of the spots on cellulose photographs are consistent with the cell proposed, but Pólányi has observed certain exceptions. Whether these are due to lattice disturbances or to the presence of another crystalline substance cannot yet be decided, but it is very likely that the latter explanation is the correct one.

In the opinion of Herzog,[6] the conception of cellulose as a two-phase system, an amorphous phase in which crystallites are embedded, helps to explain an important part of its behaviour. In many natural fibres, *e.g.*, hemp and ramie, the chief axis of the crystal cells and of the primitive fibres of the crystallites lies fairly exactly along the fibre-axis. Microscopic investigation reveals the existence of a primary isotropic substance in which the crystallites are disposed. *X*-Rays also show the presence of a not unimportant quantity of amorphous matter, probably amorphous cellulose. Jancke has shown, from a large number of *X*-ray photographs of bark fibres, that the dimensions of the crystallites in two directions are about 112 and 66 Å.U., respectively, with the third dimension somewhat similar. It is noteworthy that this observed crystallite size is of the same order as that found, by diffusion experiments, for cellulose micelles, *i.e.*, the particle size is conserved during the crystallisation process.

In the deformation of metals by cold-working, hardening is produced by gliding and crumpling of the glide-plane systems, but in cellulose the corresponding hardening does not seem to depend on any change in the crystallites, but rather on a flow and their more uniform distribution in the inter-crystalline substance caused by the application of stress to the two-phase system. That the plastic deformation depends substantially on this flow is evidenced by the

[6] *Ber.*, 1925, **58**, [*B*], 1254; *A.*, i, 1045.

close connexion between the stretching processes, quantities such as the breaking-stress, and the water-content of the material tested. The greater the swelling, the more pronounced the flow; and this fact is independent of whether or not the original material exhibits fibre-structure. Extension brings about a very small increase in the alignment of the crystallites, but films show no such effect on pressure or rolling.

Cellulose which has been mercerised (treated under tension with strong caustic soda solution, and subsequently washed) gives rise to a rather different *X*-ray diagram from that of native cellulose. The lattice is very slightly increased, although the density remains practically the same. Herzog [7] argues from this that there is a chemical rearrangement in the molecule (without increase of molecule size) of the crystalline constituent or constituents. The mercerisation process can be easily followed by means of *X*-rays, and the mechanical and *X*-ray changes do *not* run parallel. J. R. Katz and H. Mark have studied the swelling and mercerisation of cellulose,[8] etc. The swelling of cellulose, fibroin, and chitin in water and of cellulose (ramie) in aqueous solutions of zinc chloride, calcium thiocyanate, potassium iodide, and potassium iodide with mercuric iodide shows no lattice change, but in sufficiently strong solutions of the hydroxides of sodium, potassium, and lithium, or of ammoniacal copper oxide, a new *X*-ray diagram is produced. An enlargement up to 4% may be observed. All artificial silks,[9] with the exception of "acetate-silk," give rise to the same *X*-ray photograph as that of mercerised cellulose. "Cuprammonium-silk" in particular, because of its fairly definite fibre-structure, shows this effect well.

Chitin [7] from various sources and silk-fibroin [10] from nine different types of silk have also been examined by *X*-rays. The results are similar to those for cellulose, that is, the crystallites are oriented with a crystal-axis approximately parallel to the fibre-axis and are embedded in a cementing substance ("Kittsubstanz"); they possess rhombic or nearly rhombic symmetry and are based on unit cells of the usual order of magnitude containing the substance of four of the chemical groups given by the empirical formulæ. Herzog [7] gives an interesting comparison:

	Cellulose.	Silk-fibroin.	Chitin.	Tetraphenyl-urea.
Cell in (Å.U.)^3	680	675	*ca.* 1900	1965
nM	653	500–660	*ca.* 1600	1467

[7] *Naturwiss.*, 1924, **12**, 955 *et seq.*

[8] *Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 520; *A.*, 1925, ii, 666; *Z. physikal. Chem.*, 1925, **115**, 385; *A.*, ii, 660; *Z. Elektrochem.*, 1925, **31**, 105; *A.*, i, 640; *Cellulosechemie*, 1925, **6**, 35, 37; *A.*, i, 639, 640.

[9] R. O. Herzog and H. W. Gonell, *Kolloid-Z.*, 1924, **35**, 201.

[10] R. Brill, *Annalen*, 1923, **434**, 204.

The results in the last column, given for purposes of comparison, are due to Mark. The quantity nM is the product of the number of molecules per cell and the molecular weight. If these unit cells are correct, it certainly appears as if the respective true molecular weights are *not* very high multiples of the simplest empirical molecular weights.

The röntgenographic comparison of plant- and animal-cellulose [7,11] has yielded a result of chemical interest. The animal-cellulose tunicin gives rise to a powder diagram in which the six interference rings are identical in position and intensity distribution with the rings obtainable from plant-cellulose (ramie). This observation confirms what has been known to chemists for some time, that these two celluloses are either identical or very nearly so. A photograph of lichenin showed no such agreement.

Growth and Deformation Structures in General.

The substances briefly described above are more or less familiar examples of that large class of crystalline structures which has received the name of "growth-structures" ("Wachstumsstrukturen"). These structures are crystal-aggregates which are characterised by the property of a statistical anisotropy in their physico-chemical behaviour. *X*-Rays show in the clearest possible way that they are built up of crystallites arranged, not as in a quasi-isotropic medium with complete irregularity, but according to a plan in which some chief crystallographic direction coincides more or less exactly with an important direction in the structure. They recall at once such typical structures as fibres, cellulose, silk, chitin, muscle, tendon, hair, electrolytic precipitates, etc. Scarcely to be considered apart from these growth-structures is the class which may be described as "deformation-structures," as examples of which may be quoted hard-drawn metal wires, rolled foils, and plastically deformed polycrystals in general. In the realm of geology and among the framework and skeleton structures of biology are numerous types of this statistical anisotropy of crystal-aggregates. The nature of a few of the most important or interesting may here be indicated.

The simplest case is the ordinary fibre structure associated with threads of naturally grown cellulose and other fibrous substances. In this type the crystallites are all oriented so that one of the edges of the unit cell lies parallel to the fibre-axis, *i.e.*, the direction of fastest growth. A powder-photograph with the *X*-rays perpendicular to the fibre-axis becomes thus specialised into a rotation-photograph about the fibre-axis, and since this is a chief crystallo-

[11] R. O. Herzog and H. W. Gonell, *Z. physiol. Chem.*, **1924, 141, 63.**

graphic direction, the spots lie on the usual series of hyperbolæ, ($hk0$), ($hk1$), etc. From these hyperbolæ the primitive translation of the crystal-lattice which lies parallel to the fibre-axis is accurately determined and the other two axes are estimated more or less correctly according to the degree of perfection of the photograph. A very definite example of this type is afforded by the various kinds of asbestos. For instance, in anthophyllite,[12] the b-axis lies accurately parallel to the fibre-axis and is 5·27 Å.U. long. The other two axes are $a = 8{\cdot}7$ Å.U. and $c = 12{\cdot}40$. The crystal-aggregates of benzene also constitute an important growth-structure. Here we observe without ambiguity that $c = 6{\cdot}8$ Å.U., and, with great probability, that $a = 7{\cdot}6$ Å.U. and $b = 9{\cdot}6$ Å.U. In general, the direction of fastest growth in a growth-structure corresponds to the shortest edge of the unit-cell. (Cellulose appears to be an exception to this rule.) There are many variations and complications of this simple fibre-structure, *e.g.*, ring-fibres, spiral-fibres, the various forms of crossed fibres, etc. The theory and method of detection of these have been discussed very thoroughly by Pólányi, Weissenberg, and Mark,[13] whilst many instructive examples of them have been examined experimentally by Herzog and Gonell.[14] Of course, much can be learned of these structures by purely optical means, in which connexion W. J. Schmidt's "Die Bausteine des Tierkörpers im polarisierten Lichte" (Bonn, 1924) should be mentioned, but X-rays have opened up immense fields in this direction. Many substances, hitherto held to be amorphous, have proved to be either micro-crystalline or mixtures of crystals and true amorphous gels. Schmidt examined the spines of the sea-hedgehog in polarised light and observed simultaneous extinction. His deduction of single crystals has been beautifully confirmed by a Laue photograph. Similarly, the calcareous needles of certain sponges have proved to be "bio-crystals." These examples represent one extreme, but all the various degrees of orientation, from single crystals to completely irregular polycrystals, have been encountered, and investigated to a certain extent. The "simple fibre structure" represents the stage of development next below that of the true single crystal, then come the numerous types of "multiple fibre structure," an example of which is the enamel of teeth. Herzog and Gonell [14] give an X-ray picture of the enamel

[12] H. Mark, *Z. Krist.*, 1925, **61**, 75.

[13] K. Weissenberg, *Z. Physik*, 1921, **8**, 20; *Z. Krist.*, 1925, **61**, 58; M. Pólányi, *Z. Physik*, 1921, **7**, 149; *Z. Krist.*, 1925, **61**, 49; H. Mark, *ibid.*, 1925, **61**, 75.

[14] *Kolloid-Z.*, 1925, **36**, 44; *Naturwiss.*, 1924, 1153; *Ber.*, 1925, **58**, [*B*], 2228

of pig's teeth. It shows resemblances with the photograph of a rolled foil, the most familiar type of multiple fibre structure.

A remarkable group of growth-structures is that of electrolytic precipitates.[12, 15] In this case, the results are influenced considerably by the experimental conditions such as current density, the nature of the electrolyte, of the cathode, and of foreign substances introduced into the electrolyte. For instance, copper may be deposited from acid copper sulphate solution so that the [011] axis stands perpendicular to the cathode-plane, but no orientation is observable if a solution of potassium cyanide and copper acetate is used. Similarly, silver separates irregularly from a silver–potassium cyanide solution, whilst in silver deposited from $N/10$-silver nitrate at a current density of 0·010 amp./cm.^{2} [111] and to a lesser degree [100] appear as "fibre-directions." If now the current density is increased to 0·022 amp./cm.^{2}, the statistical anisotropy disappears entirely. An experiment on "sputtered" platinum did not yield a definite fibre-diagram and was not followed up.

A well-known growth-structure, which is possibly also a natural deformation-structure, is that of graphite. Hassel and Mark last year examined it by X-rays and found that the basal plane may be anywhere up to 30° on either side of the plane of the flakes. The chief growth-direction in the plane of the flakes is parallel to the direction [010] (orthohexagonal indices) with a spreading of $\pm 30°$ perpendicular to the plane and $\pm 10°$ in the plane. This is an instructive example of the way in which X-rays not only reveal statistical anistropy, but also may be used to determine the nature and degree of deviation from the ideal structures to which the natural approximate. A useful way of representing graphically the anisotropy and the observed spreading has been described by F. Wever.[16]

As a final example of growth-structure we may mention pearl and mother-of-pearl. Dauvillier [16a] has shown that natural pearls give X-ray photographs corresponding to the ordinary powder diagram, whilst mother-of-pearl (nacre) gives diffuse Laue spots. This observation affords a means of discriminating between natural and artificial (Japanese) pearls. The latter are grown round a nucleus of nacre. Thus, on taking an X-ray photograph of an artificial pearl we obtain *both* the powder diagram and the diffuse Laue spots. Shaxby [16a] has continued these investigations of Dauvillier. He has confirmed his results that, with mother-of-pearl, a pseudo-hexagonal diagram is obtained when the X-rays are

[15] Glocker and Kaupp, *Z. Physik*, 1924, **24**, 121; R. M. Bozorth, *Physical Rev.*, 1925, **26**, 390; *A.*, ii, 1038.

[16] *Z. Physik*, 1924, **28**, 69.

[16a] A. Dauvillier, *Compt. rend.*, 1924, **179**, 817; J. H. Shaxby, *ibid.*, p. 1602; *A.*, 1925, ii, 93; *Phil. Mag.*, 1925, **49**, 1201.

incident normal to the laminations, but a rectangular pattern when they fall parallel to the laminations. The observed spacings, too, agree with certain of those found by W. L. Bragg and Wyckoff for aragonite. There seems little doubt that the calcium carbonate that forms the basis of pearl and of mother-of-pearl is in the form of aragonite (orthorhombic : pseudo-hexagonal).

Much of our knowledge of the nature of deformation structures and processes has been obtained through the study of strained metals. An enormous amount of work has been carried out in this direction, and it is impossible in this place to do more than hint at the mass of results and the far-reaching deductions that have been made from them. Briefly we may say that distortion of an originally quasi-isotropic crystal-aggregate leads to a statistical anisotropy in the physico-chemical properties. An orientation of the crystal parts takes place which is at once revealed by *X*-ray examination. In ordinary technical experience, these effects, of course, are produced and studied in the polycrystalline masses which constitute metals in everyday use, but the most illuminating observations and ideas have been obtained from the examination of the effect of stress on large single metallic crystals. The theory evolved from these results has been applied to the problem of metallic crystal aggregates with great success. It is true that the simple uni-crystal theory does not explain everything that is observed in the deformation of crystal aggregates, but it undoubtedly clears up the major part of the problem. An instructive paper by Weissenberg [17] will well repay reading. What happens when a uni-crystalline wire, for instance, is stretched is that gliding takes place in the systems of glide-planes, and these are at the same time rotated more and more towards parallelism to the direction of extension. Simultaneously, the cross-section of the wire is changed from a circle to an ellipse and characteristic striations appear on its surface. Should there be more than one type of glide-system present in the wire (as is generally the case), these function in turn according to the values of the limiting stresses required to activate those most favourably placed. The final result for infinite extension is that two of the glide-systems take up positions which are symmetrical with respect to the axis of extension. For instance, in the extension of a face-centred cubic metal the chief glide-planes are the octahedra (111), whilst the chief glide-directions are the face-diagonals [110]. On careful extension, the zone-axis [112], which lies symmetrically between two of the glide-systems, tends to set itself parallel to the axis of extension. Such a result was approximately realised by G. I. Taylor and C. F. Elam [18] in the extension of an aluminium crystal. On the other

[17] *Z. Krist.*, 1925, **61**, 58.

[18] *Proc. Roy. Soc.*, 1923, *A*, **102**, 643.

hand, Ettisch, Pólányi, and Weissenberg [19] found [111] and [100] as end-directions for an Al-*poly*crystal, but Pólányi has shown that this is probably a consequence of the fact that in a mass of crystals there are frictional causes which involve a definite overstepping of the limiting stresses of the two most favourably placed glide-systems, with the result that all possible glide-systems function more or less and try to arrange themselves so that the complete set of them is symmetrically disposed about the axis of extension.

Similar conclusions hold for the processes which take place when metal foils are rolled. For rolled foils of aluminium, silver, copper, gold, and platinum,[20] the (110) plane approximates to the plane of rolling and the [112] axis to the direction of rolling. For rolled tungsten foil (body-centred), the corresponding plane and direction were found by Gross to be (100) and [110], respectively. All these effects of cold-working can be studied directly by *X*-rays. In the initial quasi-isotropic state, an *X*-ray photograph of a metal consists of simple Debye rings (powder photograph), but after cold-working a statistical anisotropy in the arrangement of the crystallites has been brought about which shows itself by a characteristic change in the *X*-ray diagram. A true powder photograph postulates all possible orientations of crystallites, so that all planes may be in a position to reflect *X*-rays. Such a condition does *not* hold after cold-working, since certain crystal directions have been favoured during the process. The consequence is that the Debye rings, uniform throughout in the photograph of an unworked metal, become discontinuous and show now as a symmetrical distribution of light and dark patches. Fig. 3, which is a photograph of a rolled gold foil taken on a cylindrical film co-axial with the primary beam of *X*-rays, and is reproduced from Mark's paper,[12] shows clearly the effect described.

As is well known, the cold-working of metals brings about marked changes in their properties, notably in their hardness. It was originally proposed by Tammann (" Lehrbuch der Metallographie ") that the cause of this hardening lay in the translations and rotations of the glide-planes as outlined above, but it seems difficult to explain all the hardening in this way. Various other suggestions have been put forward to supplement the " translation theory," *e.g.*, a destruction of the lattice and the formation of a thermodynamically unstable state (by Czochralski); an " amorphous layer " (by Beilby and Rosenhain); " local disturbances " (by Ludwik); and " hidden elastic strains " (by Heyn). But the observations and

[19] *Z. Physik*, 1921, **7**, 181.

[20] N. Uspenski and S. Konobejewski, *ibid.*, 1923, **16**, 215; H. Mark and K. Weissenberg, *ibid.*, 1923, **14**, 528; **16**, 314.

considerations of Pólányi and Gross lead to the assumption that, in the super-elastic deformation of a crystal, there takes place a splitting into thin layers which can glide over one another and have been definitely shown by *X*-rays to undergo bending. A special difficulty is inherent in this picture of the process, in virtue of the circumstance that in the most strongly stretched outer layers the individual glide-planes lie immediately against those glide-planes which are most shortened in the neighbouring element. Gross supposes from this that small holes would actually arise, but he assumes that they are filled up by a fine folding of the surfaces of the glide-planes which makes them wave-like and uneven. This folding has in fact been observed.[21] We may picture the mechanism of cold-working thus, that there takes place a gliding along the glide-planes, generally accompanied by elastic bending of the gliding lamellæ and a rotation of the crystal-elements into a certain orientation related to the chief deformation direction. The hardening is in the first place due to elastic bending of the glide-packets and the consequent fine folding in the glide-planes. This it is which hinders further slipping. The hardening by rotation must be considered to be of secondary importance.

An interesting outline of the recent investigations on deformation and recrystallisation has been contributed by F. Korber.[22] There are many other papers worthy of discussion, but space forbids.[23]

Other Inorganic Structures.

Solid carbon dioxide [24] *and solid ammonia.*[25] Solid carbon dioxide is cubic and at liquid-air temperature the unit cell, which contains four molecules, has a side of 5·62 Å.U. The structure deduced has the symmetry of pyrites, (T_h^6). The molecules lie on non-intersecting triad axes, each carbon atom between the two oxygen atoms belonging to it. The arrangement is apparently a non-ionised one. It should be compared with the cubic form (β-cristobalite) of silica

[21] Mark, Pólányi, and Schmid, *Z. Physik*, 1923, **12**, 115.

[22] *Stahl u. Eisen*, Febr. 12th and 19th, 1925.

[23] C. Benedicks, *Nature*, 1925, **115**, 230; *A.*, ii, 188; E. Schiebold, *Z. Metallk.*, 1924, 417, 462; *A.*, 1925, ii, 186; J. Czochralski, *ibid.*, 1925, **17**, 1; *A.*, ii, 186; H. Röhrig, *ibid.*, 1925, **17**, 63; *A.*, ii, 282; R. Glocker, *Z. Physik*, 1925, **31**, 386; *A.*, ii, 272; M. Pólányi, *Z. Metallk.*, 1925, **17**, 94; *A.*, ii, 370; G. Sachs, *ibid.*, p. 85; *A.*, ii, 370; G. I. Taylor and C. F. Elam, *Proc. Roy. Soc.*, 1925, *A*, **108**, 28; M. Pólányi and E. Schmid, *Z. Physik*, 1925, **32**, 684; *A*, ii, 752; C. F. Elam, *Phil. Mag.*, 1925, **50**, 517; *A.*, ii. 945; *J. Iron Steel Inst.*, Sept., 1925; *A.*, ii. 946; *Proc. Roy. Soc.*, 1925, *A*, **109**, 143; *A.*, ii, 954.

[24] J. De Smedt and W. H. Keesom, *Proc. Roy. Acad. Sci. Amsterdam*, 1924, **27**, 839; H. Mark and E. Pohland, *Z. Krist.*, 1925, **61**, 293.

[25] H. Mark and E. Pohland, *ibid.*, p. 532.

which has recently been analysed. In carbon dioxide, the three atoms are collinear, but in silica each silicon atom is surrounded by a tetrahedron of oxygen atoms. Solid ammonia also is cubic between —77° and —160°. The cell again contains four molecules and has a side of 5·19 Å.U. The nitrogen atoms lie on non-intersecting triad axes with the space-group T_4. Three hydrogen atoms must be arranged trigonally about each nitrogen atom, but probably do not lie in the same plane with it.

Barytes ($BaSO_4$).[26] The rhombic holohedral cell ($a = 8·89$, $b = 5·45$, $c = 7·17$ Å.U.—Wyckoff) contains four molecules of $BaSO_4$ and has the symmetry of Q_h^{16}. It is not pseudo-hexagonal like aragonite. There is evidence from the intensity measurements that the SO_4 group consists of a tetrahedron of oxygens round the sulphur (James and Wood), whilst according to Mark the metal atoms are not surrounded by equidistant anions, but each metal is closely related to one particular anion. Strontium and lead sulphates, and potassium permanganate and perchlorate are also found to crystallise in the space-group Q_h^{16}, and anhydrous calcium sulphate in Q_h^{17}.

Diopside [$CaMg(SiO_3)_2$].[27] The monoclinic prismatic cell has dimensions $a = 9·71$, $b = 8·89$, $c = 5·24$, $\beta = 105° 50'$. There are four molecules per cell and the space-group is C_{2h}^6.

Manganese.[28] Manganese, until last year, resisted all attempts at *X*-ray analysis of its structure. This has proved to be due to the fact that, as ordinary manganese, it always consists of a mixture of allotropes. Three modifications have been identified. One of them (the γ-form of Westgren, the α-form of Bradley) has been obtained only by electrolytic deposition. It is face-centred tetragonal (four atoms per cell) with $a = 3·77$ and $c = 3·53$ Å.U. Westgren considers it possible, although improbable, that it is in reality a hydride, but if it is pure manganese it gives a calculated density of 7·21. It is apparently stable only at low temperatures, being converted by heat into the other two forms. This change does not appear to be reversible. According to Westgren and Phragmén, the allotrope stable at the ordinary temperature (they call it α-manganese) is cubic, $a = 8·89$, with 56 atoms per cell. The calculated density is the same as that of the electrolytic form. At higher

[26] R. W. James and W. A. Wood, *Proc. Manchester Phil. Soc.*, 1924—25, **69**; Rinne, Hentschel, and Schiebold, *Z. Krist.*, 1925, **61**, 164; L. Pauling and P. H. Emmett, *J. Amer. Chem. Soc.*, 1925, **47**, 1026; *A.*, ii, 485; R. W. G. Wyckoff and H. E. Merwin, *Amer. J. Sci.*, 1925, **9**, 286; *A.*, ii, 485; H. Mark, *Z. Elektrochem.*, 1925, **31**, 523; *A.*, ii, 1130.

[27] R. W. G. Wyckoff and H. E. Merwin, *Amer. J. Sci.*, 1925, **9**, 379; *A.*, ii, 485.

[28] A. Westgren and G. Phragmén, *Z. Physik*, 1925, **33**, 777; *A.*, ii, 1035; A. J. Bradley, *Phil. Mag.*, 1925, **50**, 1018; *A.*, ii, 1124.

temperatures, it changes to (Westgren's) β-form, which also is cubic (a = 6·29 or 12·58) with 20 or 160 atoms per cell, the corresponding density being 7·29. Carbon dissolves in manganese in the same way as in γ-iron, *i.e.*, not by replacing metal atoms, but by penetrating into the lattice spaces between them.

Lithium potassium sulphate ($LiKSO_4$).[29] The symmetry corresponds to the hexagonal space-group C_6^6, a = 5·13 and c = 8·60 Å.U. There are two molecules of $LiKSO_4$ per cell. The potassium atoms are situated on a simple hexagonal lattice of axial ratio, $a : c$ = 1 : 0·838. The sulphate ions comprise two simple hexagonal lattices of axial ratio, $a : c$ = 1 : 1·6755, which fit together as if the sulphate ions were spheres in hexagonal close-packing. The lithium ions alternate with the sulphate ions. Each sulphate ion is surrounded by six potassium atoms, and each potassium atom by six sulphate ions. Each sulphur atom is surrounded tetrahedrally by four oxygen atoms. The observed axial ratio of the structure is almost the theoretical value for hexagonal close-packing. It appears from this as if the size of the unit is determined by the size of the sulphate ions alone, the metal atoms simply filling up as far as possible the interstices of the structure.

Copper–zinc, silver–zinc, and gold–zinc alloys.[30] As a result of the *X*-ray study of ten binary systems of alloys, Westgren and Phragmén have drawn the conclusion that the suggestions put forward to date on the true difference between chemical compounds and solid solutions are not based on sound arguments. In their opinion, the fundamental difference between solid chemical compounds and solid solutions lies in their structure, that in an ideal chemical compound structurally equivalent atoms are chemically identical, whilst in an ideal solid solution all atoms are structurally equivalent. These two structures represent extreme types, the former being comparatively rare in metallic phases. Most phases seem to lie in the region between the two extreme types, forming what might be characterised as solid solutions in chemical compounds. *X*-Rays have shown that in the copper–zinc, silver–zinc, and gold–zinc systems there are five different types of structure common to all three. Two additional phases have been found in the gold–zinc system. The five common systems, arranged according to increasing zinc content, are: α, face-centred cubic; β, cæsium chloride structure; γ, cubic with 52 atoms per cell; ε, close-packed hexagonal, axial-ratio 1·55—1·60; η, close-packed hexagonal, axial-ratio, 1·80—1·90. A gold–zinc (γ′) phase with 50% of zinc was cubic with probably 32 atoms per cell; another phase (γ″), 53—54%

[29] A. J. Bradley, *Phil. Mag.*, 1925, **49**, 1225; *A.*, ii, 638.
[30] A. Westgren and G. Phragmén, *ibid.*, **50**, 311; *A.*, ii, 746.

Zn, appeared also to be cubic with about 90 atoms per cell. In accordance with the definitions, the α-, η-, and probably the ε-phases represent ideal solid solutions, the first one having copper, silver, gold, and the last two zinc as solvent. The other phases may be regarded as solid solutions in chemical compounds. The solvents of the β-phases are CuZn, AgZn, and AuZn.

Other Organic Structures.

Ethane and diborane, C_2H_6 and B_2H_6.[31] *X*-Ray powder photographs of these two compounds in the solid state have shown that structurally they are very similar. There seems to be no doubt that boron in diborane, like carbon in ethane, functions as a quadrivalent element. They are both hexagonal with two molecules per cell. The centres of gravity of the molecules are arranged in hexagonal close-packing, the molecules themselves possessing at least three-fold symmetry. The distance between carbon atoms of the same molecule is about 1·55 Å.U., and about 3·5 Å.U. between carbon atoms of neighbouring molecules. The corresponding numbers for diborane are 1·85 Å.U. and 3·7 Å.U. The molecules in the crystal correspond to the ordinary chemical molecules.

Long-chain compounds.[32] The *X*-ray investigation, described in a previous Report, of these compounds has been continued, with many interesting results. The situation has been considerably clarified by the discovery that the crystals are mostly monoclinic or triclinic. As a consequence of this observation it has been decided that the long spacing so prominent in photographs of chain compounds does not represent the true length of the molecule. The carbon chains are in general inclined to the basal plane of the unit cell, and although the increase in observed spacing per carbon atom is linear, this regular change is merely the projection of the alteration in length of the carbon chain on the normal to the basal plane. Stearic acid crystals, for instance, are monoclinic, $a = 5·60$, $b = 7·38$, $c = 50·9$ Å.U., $\beta = 59·7°$, with four molecules per cell and density rather above 1·05. The crystal habit appears to consist simply of {001} and {110}. Stearolic acid appears to be triclinic, whilst for the normal hydrocarbons the orthorhombic system seems to be indicated. Ten of the latter,[33] between C_{17} and C_{35}, have been investigated. The increase per carbon atom for the long spacing is 1·3 Å.U., a value considerably higher than that predicted from the theory put forward by Müller and Shearer. Octadecane and eicosane exist in two crystalline modifications. Sixteen aliphatic ketones,[34]

[31] H. Mark and E. Pohland, *Z. Krist.*, 1925, **62**, 103.

[32] A. Muller, *Nature*, 1925, **116**, 45; *A.*, ii, 748; R. W. G. Wyckoff and H. E. Merwin, *Science*, 1925, **61**, 613; *A.*, ii, 1129.

[33] A. Müller and W. B. Saville, *J.*, 1925, **127**, 599.

[34] W. B. Saville and G. Shearer, *ibid.*, p. 591.

between C_{13} and C_{35}, have also been examined. These fall into two sets, the increase per carbon (linear in both cases) being greater for the methyl ketones than for the others. The results confirm the view that the active group, $\cdot CO \cdot CH_3$, produces a tendency for the molecules to arrange themselves end to end in pairs, and also show that although the position of the $\cdot CO \cdot$ group has no effect on the length of the molecule, it has a powerful effect on the intensity distribution, a property which Shearer [35] has successfully applied to the problem of localisation of such groups. R. E. Gibbs [36] has measured the spacings of fatty acids which are liquid at the ordinary temperature. At hexoic acid deviations from the linear law appear and increase gradually down to propionic acid, an abrupt change occurring at acetic acid. This corresponds to the changes observed in the freezing points.

Inquiries similar to those outlined above are being carried out by other investigators [37] also, with similar results. J. J. Trillat [38] has applied the method to the examination of thin films of oleic, linoleic, and linolenic acids, containing one, two, and three double linkings, respectively. He has observed the changes which take place on oxidation at these linkings .

Iodosuccinimide.[39] The unit cell of this compound contains the substance of four chemical molecules and exhibits, *not* the symmetry of the ditetragonal pyramidal class (as was hitherto believed), but that of the tetragonal pyramidal (enantiomorphous) class. The *X*-ray observations have been supplemented by a detailed crystallographic and optical re-examination by Tutton,[40] who has found that the substance is optically active, although it was not possible to determine the angle of rotation.

Calcium formate.[41] The crystals are orthorhombic bipyramidal and not bisphenoidal, as was suggested by Plathan. The unit cell contains eight molecules, $a = 10{\cdot}19$, $b = 13{\cdot}41$, $c = 6{\cdot}27$ Å.U. Space-group Q_h^5.

Maleic and fumaric acids.[42] In the monoclinic prismatic cell of maleic acid there are four asymmetric molecules. The crystals can be bent and twisted in certain directions without fracture, and

[35] *Proc. Roy. Soc.*, 1925, *A*, **108**, 655; *A.*, ii, 938; R. Robinson, *Nature*, 1925. **116**, 45; *A.*, ii, 745.

[36] *J.*, 1924, **125**, 2622.

[37] E. Friedel, *Compt. rend.*, 1925, **180**, 269; *A.*, ii, 186; J. J. Trillat, *ibid.*, p. 280; *A.*, ii, 1951; G. Friedel, *ibid.*, p. 409; *A.*, ii, 272; J. J. Trillat, *ibid.*, p. 1329, 1838; *A.*, ii, 489, 752.

[38] *Ibid.*, 1925, **181**, 504; *A.*, ii, 1127.

[39] K. Yardley, *Proc. Roy. Soc.*, 1925, *A*, **108**, 542; *A.*, ii, 746.

[40] *Ibid.*, p. 548; *A.*, ii, 747.

[41] K. Yardley, *Min. Mag.*, 1925, **20**, 296; *A.*, ii, 430.

[42] *Idem*, *J.*, 1925, **127**, 2207.

twinning takes place with great facility on the (100) plane. The characteristic features of this twinning are explained very reasonably if the molecules actually in the twin plane are slightly different from those in the body of the structure—plano-symmetrical, in fact. Chemistry would suggest such a symmetry for the "free molecules," from which the twins commence to grow symmetrically outwards. The space-group is C_{2h}^5 and a structure has been suggested to explain the main *X*-ray results. Fumaric acid, which has hitherto defied crystallographic examination owing to the very complex twinning, etc., has yielded the result that it is anorthic with six molecules per cell. Its crystallographic data have been determined solely by the Bragg spectrometer. It should be noted that the unit cell contains three times as many molecules as are required to produce triclinic pinakoidal symmetry, but examination of certain of its derivatives [43] does not indicate association in the solid state for any other case.

Pentaerythritol tetranitrate.[44] This is built on a simple tetragonal lattice of space-group D_{4h}^7 with four chemical molecules per cell. The molecule appears to possess rhombic pyramidal (C_{2v}) symmetry, one dyad axis parallel to the *c*-axis, which is the intersection of two planes of symmetry, (100) and (010).

Miscellaneous.

Monoclinic Thallium Nickel and Thallium Cobalt Sulphates.[45]—A full crystallographic examination has shown that these salts are true members of the isomorphous series of monoclinic, hexahydrated, double sulphates and selenates, $R_2M(SO_4)_2,6H_2O$.

Non-magnetic Films of Nickel.[46]—Nickel films have been prepared, by spattering in hydrogen, which are initially non-magnetic, but become magnetic when heated to 300—400°. *X*-Rays show the ordinary face-centred lattice for the magnetic films, but the non-magnetic films are apparently amorphous. From this result it is difficult to avoid the conclusion that the ferro-magnetism of nickel is a property, not of the individual atom, but of the crystal-aggregate.

Non-existence of the Clark-Duane Secondary X-Ray Spectra.[47]—In a previous Report were mentioned some experiments of Clark and Duane which were claimed to have revealed the existence of *X*-ray spectra in addition to those ordinarily found. Some of these

[43] K. Yardley, *Phil. Mag.*, 1925, **50**, 864; *A.*, ii, 1033.

[44] I. E. Knaggs, *Min. Mag.*, 1925, **20**, 346; *A.*, ii, 748.

[45] A. E. H. Tutton, *Proc. Roy. Soc.*, 1925, *A*, **108**, 240; *A.*, ii, 749.

[46] L. R. Ingersoll and S. S. De Vinney, *Physical Rev.*, 1925, **26**, 86; *A.*, ii, 846.

[47] A. P. Weber, *Z. Physik*, 1925, **33**, 767; *A.*, ii, 1034; A. H. Armstrong, W. Duane, and R. J. Havighurst, *Proc. Nat. Acad. Sci.*, 1925, **11**, 218; *A.*, ii, 1033; H. Kulenkampff, *Physikal. Z.*, 1925, **26**, 657; *A.*, ii, 1033.

spectra obeyed the Bragg law, whilst some were entirely anomalous. Neither type was ever satisfactorily explained, although a partial explanation, based on our knowledge of X-ray absorption spectra, was put forward by W. Kossel.[48] Many workers have tried to reproduce Clark and Duane's results, but without success. There seems little doubt now that it is a spurious effect due to imperfections in the crystals used. Careful work on very perfect alkali halide crystals has proved that there is no anomalous reflexion of X-rays characteristic of the constituent elements of the crystals. Furthermore, it has been shown that the structures of cæsium tri-iodide and cæsium dibromoiodide deduced from these supposed secondary spectra are incorrect.[49]

Etched Figures.[50]—After discussing the kinetics of the dissolution of a crystal, Tammann outlines a theory of the orientation of etched figures. According to this, the crystal surface is first attacked along the lines of the crystal lattice in which the atoms entering into the reaction are most closely packed. As the etching continues, figures are produced the outlines of which are parallel to the primary grooves. A number of experimental cases are analysed, and on the whole the agreement with theory is remarkably good. A very ingenious application of the study of etched figures has been made by S. I. Tomkeiev [51] to the elucidation of the structure of aragonite. He has obtained striking quantitative agreement between the observed etched figures and the structure he proposes for aragonite. Strange to say, this structure is in direct conflict with X-ray data, and it cannot be harmonised with the structure recently obtained independently by W. L. Bragg and R. W. G. Wyckoff. In spite of arguments based on the etched figure, the conclusion seems unavoidable that Tomkeieff's structure is incorrect.

Influence of Atomic Arrangement on Refractive Index.[52]—In a previous Report it was described how a successful attack has been made on the problem of the calculation of the refractive indices of crystals from refractivity data. This work has now been extended. The indices of calcite, aragonite, and alumina have been calculated on the assumption that the atoms composing the crystals are ionised, and that each type of atom, when polarised by the electric force of the incident radiation, acts as an electrical doublet

[48] *Z. Physik*, 1924, **23**, 278.

[49] R. M. Bozorth and L. Pauling, *J. Amer. Chem. Soc.*, 1925, **47**, 1561; *A.*, ii, 748.

[50] G. Tammann, *Z. anorg. Chem.*, 1925, **146**, 413, 420; *A.*, ii, 942.

[51] *Min. Mag.*, 1925, **20**, 408; *A.*, ii, 1035.

[52] W. L. Bragg, *Proc. Roy. Soc.*, 1924, *A*, **106**, 346; *A.*, 1925, ii, 92; K. Fajans and G. Joos, *Z. Physik*, 1924, **23**, 1.

with a characteristic moment. It is also shown that it may be possible later to reverse the process and deduce atomic arrangement from optical data.

Atomic Structure Factor in the Intensity of X-Ray Reflexion by Crystals.[53]—In this paper Hartree has attempted to give quantitative expression to the change in scattering power of atoms with change in glancing angle. It is clear that in dealing with the change in intensity of *X*-ray reflexion by crystals as the glancing angle increases, we are not justified in assuming that all atoms are equivalent and subject to the same numerical adjustment. Hartree has made an analysis of the problem and from his conclusions drawn up tables of " F-factors " which are to be applied to the various types of atoms taking part in the *X*-ray reflexion. For the sodium and chlorine ions the theoretical values are larger than the observed, and probably the tables as a whole need modification to allow for the influence of certain obscure causes. These points are discussed by W. L. Bragg [54] in the communication succeeding Hartree's.

W. T. Astbury.
W. H. Bragg.

[53] D. R. Hartree, *Phil. Mag.*, 1925, **50**, 289; *A.*, ii, 735.
[54] *Ibid.*, 306; *A.*, ii, 735.

MINERALOGICAL CHEMISTRY.

Geochemistry.

Bischof's classical work on "Chemical Geology" dating from 1847, seems to have been almost forgotten, but there is now a revival in the study of this comprehensive subject under the name "Geochemistry." Recent books are: a new (fifth) edition of F. W. Clarke's well-known "Data of Geochemistry" [1]; W. Vernadsky, "La Geochimie" (Paris, 1924); and, in Russian, A. E. Fersman, "Geochemistry of Russia." [2] The readable and very suggestive book by Vernadsky contains the following chapters: I, General considerations on geochemistry; II, Silicon as silicates in the earth's crust; III, Carbon and living matter; IV, The radioactive chemical elements. Fersman's book deals with "topomineralogy," the distribution of chemical elements, and the accumulation and association of elements in certain places; genetic mineralogy in relation with genetic types and cycles. European Russia is divided into twelve geochemical regions or provinces.

An elaborate paper by F. W. Clarke and H. S. Washington on "The composition of the earth's crust" [3] collects together their previous conclusions and gives the details on which these conclusions are based. The final calculations give for the average composition of the solid crust to a depth of ten miles, including also the hydrosphere and atmosphere, the following percentages: O, 49·52; Si, 25·75; Al, 7·51; Fe, 4·70; Ca, 3·39; Na, 2·64; K, 2·40; Mg, 1·94; H, 0·88; Ti, 0·58; Cl, 0·188; P, 0·12; C, 0·087; Mn, 0·08; S, 0·048; Ba, 0·047; Cr, 0·033; N, 0·030; F, 0·027; Zr, 0·023; Ni, 0·018; Sr, 0·017; V, 0·016; Ce, Y, 0·014; sum of remainder 0·042%. It is seen that 99·5% of the crust consists of thirteen elements and but few common rock-forming minerals. These, together with those listed above and some others, are classed as "petrogenic" elements. "Metallogenic" elements are Cu, Zn, Ga, Ge, As, Se, Br and the others falling below them in the periodic table; they are of sporadic occurrence and are found only under

[1] *Bull. U.S. Geol. Survey*, 1924, No. **770**, 841 pp.

[2] Part I of Vol. I (Petrograd, 1922); [*Min. Mag.* (*Abstr.*), 1925, **2**, 415]. The work is to be completed in three volumes, each consisting of several parts.

[3] *Prof. Paper U.S. Geol. Survey*, 1924, No. **127**; *A.*, 1925, ii, 63 (compare *Ann. Report*, 1923, **20**, 261).

certain conditions as workable deposits of economic value. The compounds of these two " natural " groups of chemical elements, as represented in nature by minerals, are considered in detail. Petrogenic elements form mostly oxides and oxygen-salts, whilst metallogenic elements form mostly sulphides, arsenides, and sulphosalts.

H. S. Washington wanders farther afield and considers the radial distribution of certain elements in the earth's interior.[4] From a consideration of the composition of meteorites and rocks, the velocity of earthquake waves at different depths, and the density and compressibility of minerals and rocks, he draws conclusions bearing on the distribution of matter within the earth.[5] The following zones are deduced : central core of nickel-iron, corresponding with meteoric iron (3,400 km.thick) ; lithosporic shell consisting of patches of silicates in a sponge of metal, corresponding with pallasites (700 km.) ; ferrosporic shell, corresponding with meteoric stones (700 km.) ; peridotitic shell (1,540 km.) ; basaltic shell (40 km.) ; and granitic shell or surface crust (20 km.). From the calculated chemical composition, volume, and mass of each of these zones, the composition of the earth as a whole is deduced as : Fe, 39·76 (31·82 as free metal, and 7·94 in silicates) ; O, 27·71 ; Si, 14·53 ; Mg, 8·69 ; Ni (free), 3·16 ; Ca, 2·52 ; Al, 1·79 ; S, 0·64 ; Na, 0·39 ; Co, 0·23 ; Cr, 0·20 ; K, 0·14 ; P, 0·11 ; Mn, 0·07 ; C, 0·04 ; Ti, 0·02 ; total, 100·00. It is noted that there is an excess of iron for combination with silicon and oxygen.

The chemistry of the earth's core has been further considered by L. H. Barnett,[6] his calculations being based on the known densities of the earth as a whole and its crust and of the chemical elements, together with Washington's data for the average chemical composition of the crust. An irregular core of metallic substances (" metallic fusion "), probably more or less mixed with silicates, is estimated at about 77·5% of the whole, whilst an irregular shell of silicates (" slag "), more or less mixed with metal, constitutes the remaining 22·5%. This core is estimated to consist of Fe, 90% ; Ni, Co, and Cu, 7% ; the remaining 3% including gold and platinum at 0·003%. G. Tammann considers that between the metallic core and the silicate crust there is a zone of sulphides.[7]

It is to be noted that speculations on the chemical composition of the interior of the earth are based largely on a comparison of the composition of terrestrial rocks and meteorites. We may so pass

[4] *J. Washington Acad. Sci.*, 1924, **14**, 435 ; *A.*, 1925, ii, 234.
[5] *Amer. J. Sci.*, 1925, [v], **9**, 351 ; *A.*, ii, 591. [6] *J. Geol.*, 1924, **32**, 615.
[7] *Z. anorg. Chem.*, 1924, **131**, 96 ; 1924, **134**, 269 ; *A.*, 1924, ii, 163, 493 (compare *Ann. Report*, 1923, **20**, 262).

from geochemistry to cosmochemistry. Both of these aspects of the subject are dealt with by A. E. Fersman in a small book entitled "Chemical Elements of the Earth and the Cosmos." [8] He considers the laws of distribution and migration of the chemical elements in the earth and in the cosmos, and traces a connexion between such distribution and their place in the periodic system and their atomic structure. It is pointed out that everywhere—in the earth's crust, in meteorites, the sun, planets, comets, and stars—there is a preponderance of elements of the helium atomic group, namely those with atomic weights divisible by 4 and up to atomic number 28 (Ni). P. N. Chirvinsky [9] has calculated an average composition for cosmic matter from statistical data of the weights and number of meteorites of different types that have been observed to fall on the earth's surface during the period 1492 to 1921. The percentage composition arrived at may be expressed by the formula $M_4Si_2O_7$, which may also be written as a mixture of orthosilicate, metasilicate, and free metal, $M_2SiO_4 + MSiO_3 + M$, where M is a collective metal with mean atomic weight 40·58. Metals and metalloids are present in very nearly equal proportions by weight. This is taken to represent a pseudo-element, "cosmium," with equivalent atomic weight 25·59. An interesting and suggestive essay, entitled "The evolution and disintegration of matter," has been written by F. W. Clarke.[10]

In the several recent papers descriptive of individual meteorites an outstanding feature is the discovery in 1921 of an enormous mass of meteoric iron in the desert of Adrar, at about 45 km. south-west of Chinguetti in Mauretania, French West Africa. As reported by A. Lacroix,[11] it measures 100 metres in length and 40 metres in height, and is perhaps 160,000 cubic metres in volume. Containing about 20% of silicates, it represents a new type of meteorite intermediate between the siderites and pallasites; further, the silicate portion consists largely of hypersthene rather than olivine.

Amongst the mineral constituents of meteorites, quartz has been mentioned as present in the St. Mark's meteoric stone.[12] Of the phosphates sparingly present in certain stones, it is now found that merrillite has the composition $Na_2O,3CaO,P_2O_5$, and is thus distinct from any known terrestrial mineral.[13] In one stone it was found associated with chlor-apatite. Hydrocarbons ("bitumen") have

[8] Peterburg, 1923 (in Russian); [*Min. Mag.* (*Abstr.*), 1924, **2**, 256].

[9] *Astronomische Nachrichten*, 1924, **222**, 103; [*Min. Mag.* (*Abstr.*), 1925, **2**, 389].

[10] *Prof. Paper U.S. Geol. Survey*, 1924, No. **132**-D, 51.

[11] *Compt. rend.*, 1924, **179**, 309; *A.*, 1924, ii, 693.

[12] G. P. Merrill, *Amer. Min.*, 1924, **9**, 112.

[13] E. V. Shannon and E. S. Larsen, *Amer. J. Sci.*, 1925, [v], **9**, 250; *A.*, ii. 321.

occasionally been recorded in meteorites; and the suggestion is now made that these may have been formed by the action of water on carbides after the arrival of the meteorites on the earth's surface.[14]

A problem to which some attention has lately been given, but which still remains unsolved, is that of the origin of *tektites*.[15] This general term includes the moldavites or "bottle-stone" found in river-gravels in Bohemia and Moravia. These consist of a clear glass, and being of a rich green colour they have been used as gem-stones under the names "pseudo-chrysolite" and "water-chrysolite." They are remarkable for their corrugated and deeply sculptured surfaces. At one time they were thought to be artificial, the products of an ancient glass-making industry, and this view is still held by some authors. Other kinds of tektites are the australites or "obsidianites," found in large numbers loose on the surface of the ground in certain parts of Australia and Tasmania; and the billitonites found in river-gravels and tin-gravels in Billiton and other places in the East Indies. These consist of dark green or black glass with glossy surface, and are of curious button-like, dumb-bell, and other shapes with surface markings in concentric rings. They have been thought to be of volcanic origin, the curious shapes being acquired when molten drops of lava were shot out from volcanoes. But there are no recent volcanoes in Australia. The suggestion made by F. E. Suess in 1900 that tektites are of meteoric origin was only slowly accepted, but now there are many adherents to this view. None has been observed to fall. If they did fall they evidently came down in showers, like the meteoric stones which fell at Holbrook, Arizona, in 1912, when more than 14,000 stones were picked up. The main difficulty, however, is that presented by the chemical composition of these glassy bodies. They are high in silica, 70% to 88%, with only little lime and alkalis. They thus differ in composition from artificial and volcanic glasses and very widely from any recognised meteorites.

Constitution of Silicates.

The papers on this subject are increasing in number, but it must be said that no real advance appears to be made. Various theories are being put forward and each is tested serially for different groups of minerals. Much ingenuity is displayed in attempting to explain all cases by any one theory. The mica group has been studied most, and samples of the different types of formulæ that have been proposed are quoted below.

[14] P. E. Spielmann, *Nature*, 1924, **114**, 276; *A.*, 1924, ii, 867.

[15] V. Goldschmidt, *Beitr. Kryst. Min.*, 1924, **2**, 148. A series of abstracts of recent papers in *Min. Mag.* (*Abstr.*), 1922, **1**, 406–9.

B. Gossner doubts the existence of complex molecules corresponding with the empirical formulæ of silicates, for example $KAlSi_3O_8$ for orthoclase; and he expresses the composition by the combination, analogous to double salts, of certain simple and stable molecules, such as SiO_3Ca, Al_2O_3, AlO_2H, SiO_2, etc. In addition to the papers mentioned in the last report, he has continued the series [16] with the groups of chlorites, "brittle micas," monoclinic pyroxenes and amphiboles, alkali-amphiboles, babingtonite, gehlenite–melilite group, and micas. For example, the "building scheme" (Bauplan) for the pyroxenes is based on the complex (double salt) SiO_3Mg,SiO_3Ca, in which SiO_3Mg is replaceable by Al_2O_3 or $SiO_3(Fe,Mn)$, and SiO_3Ca by SiO_3Mg. The following are some of the formulæ he gives for the micas:

Muscovite . . .	$[SiO_2,SiO_3K_2,Al_2O_3],4SiO_2,4AlO_2H.$
Biotite . . .	$[SiO_3K_2,SiO_3Mg],3SiO_3Mg,3AlO_2H.$
Lepidolite . . .	$[SiO_3K_2,SiO_3Li_2],4SiO_2,4AlOF.$

According to the theory of J. Jakob silicates are referred to the prototypes $[SiO_4]R^{I}_4$, $[SiO_5]R^{I}_6$, and $[SiO_6]R^{I}_8$, with or without added SiO_2 groups. For the micas he postulates the following "part-molecules" (Teilmoleküle):

$$\left[Al(SiO_4)_3\right]^{Al_2}_{R^{I}_3},\ \left[Al(SiO_5)_3\right]^{Al_2}_{R^{I}_9},\ [Mg(SiO_4)_3]R^{II}_5,\ [Mg(SiO_5)_3]R^{II}_8,$$

and $[Mg(SiO_5SiO_2)_3]R^{II}_8$. He gives detailed analyses, together with density and optical determinations, for eight specimens of manganophyllite (a variety of biotite containing some manganese) from Sweden.[17] As an example of the type of formula, the following (in which, curiously, manganese does not appear) is deduced from one of the analyses:

$$50{\cdot}07\left[Al(SiO_4)_3\right]^{Al_2}_{K_{2\cdot134}H_{0\cdot866}} + 39{\cdot}04\left[Mg(SiO_5)_3\right]^{Mg_{6\cdot519}}_{H_{2\cdot962}} + 10{\cdot}89\left[Mg(SiO_5SiO_2)_3\right]^{Mg_{6\cdot519}}_{H_{2\cdot962}}.$$

W. Kunitz [18] has made a noteworthy attempt to correlate the physical and optical characters with the chemical composition for minerals of the mica group. Only few data, in which all the determinations were made on the same sample of material, are available from the literature. Thirty-two new analyses were therefore made

[16] *Centr. Min.*, 1924, 97, 129, 257; 1925, *Abt. A.*, 1, 39, 73; *Z. Krist.*, 1924, **60**, 76, 302, 361; 1925, **61**, 538; *Chemie der Erde*, 1925, **2**, 103; *A.*, ii, 821.

[17] *Z. Krist.*, 1925, **61**, 155.

[18] *Jahrb. Min. Beil.-Bd.*, 1924, **50**, 365.

of micas of various kinds, and in many cases the density and optical constants were also determined. It is shown that in biotite, etc., the estimation of water is often too low, due to the reaction $2FeO + H_2O \rightleftarrows Fe_2O_3 + H_2$. To obviate this, the mineral was heated with chlorate and the gases passed over platinised asbestos. Three main isomorphous groups of micas are recognised : I, alumina-micas or the muscovite series, in which Al is replaceable to a limited extent (up to 10%) by Fe^{III}. II, magnesia-iron micas or the biotite series, in which Mg and Fe^{II} are completely replaceable. III, lithia-micas or lithionites; here a special tervalent group [2Li,Si], denoted as " Le," is completely replaceable by Fe^{II}. A summary of the results with formulæ of the hypothetical end-members is quoted below. They show that with increasing iron there is a corresponding, often linear, increase in the density and in the refractive indices. The refractive indices are to some extent also modified by the complete isomorphous replacement of F and OH. Partial isomorphous replacements are also Si—Ti, Si—Al, Al—Cr—Mn, and K—Na (but not K—H and Al—Mg, as required by some theories). All micas can be considered to contain the fundamental molecule $KAlSiO_4$ (kaliophilite) with the addition of molecules corresponding with kaolin, serpentine, and chlorites.

	End-members.	$n(\alpha)$.	$n(\beta)$.	$n(\gamma)$.	2E.	d.
Muscovite	$KH_2Al_3(SiO_4)_3$	1·5514	1·5810	1·5873	80° 40′	2·802
Al : Fe^{III} = 10 : 1	↓	1·5719	1·6105	1·6148	58 10	2·885
(not known)	$KH_2Fe^{III}_3(SiO_4)_3$	—	—	—	—	—
Phlogopite	$KH_2AlMg_3(SiO_4)_3$	1·5440	—	1·578	?	2·791
Biotite	↓	—	—	—	—	—
Lepidomelane	$KH_2AlFe^{II}_3(SiO_4)_3$	1·629	—	(1·68)	?	3·340
Lepidolite	$KH_2Al_2Le(SiO_4)_3$	1·5290	1·5520	1·5558	78 20	2·801
Zinnwaldite	↓	1·5485	1·5745	1·5792	50 6	2·97
Protolithionite	$KH_2AlFe^{II}_3(SiO_4)_3$	1·592	—	1·625	0	3·305

A. F. Hallimond [19] calculates from published analyses of the " acid " micas the molecular proportions on the basis $(Si,Ti)O_2 = 600$. In the soda- and potash-micas K_2O+Na_2O is then near 100. The molecular proportions of R_2O_3 plotted against RO give points along a line from $K_2O,3Al_2O_3,6SiO_2,2H_2O$ (muscovite) to

$$K_2O,2Al_2O_3,RO,6SiO_2,2H_2O$$

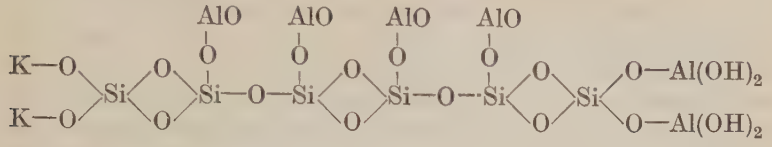
(phengite), showing a replacement of R_2O_3 by RO, as previously suggested for glauconite.[20] In the lithia-micas $SiO_2 = 600$, $K_2O = 100$, $Li_2O = 100$, and R_2O_3 plotted against RO gives two series : $K_2O,Li_2O,2Al_2O_3,6SiO_2,2H_2O$ (lepidolite) to

$$K_2O,Li_2O,Al_2O_3,RO,6SiO_2,2H_2O$$

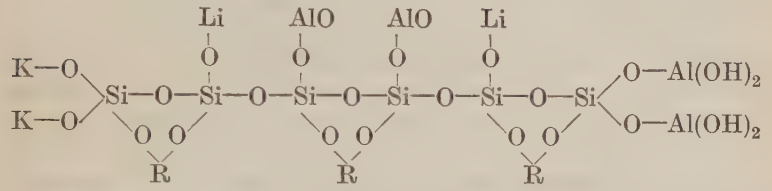
(cryophyllite), and lepidolite to $K_2O,Li_2O,2Al_2O_3,3RO,6SiO_2,2H_2O$

[19] *Min. Mag.*, 1925, **20**, 305; *A.*, ii, 819.
[20] *Ibid.*, 1922, **19**, 330; *A.*, 1922, ii, 861.

(protolithionite). Graphical formulæ are written for each of these; for example, for muscovite :



and for protolithionite :



A. N. Winchell [21] bases his studies of the mica group on the proposition that isomorphism depends on the atomic volumes of the replacing elements, rather than on their valencies—the replacing "bricks" in the crystalline structure must be of approximately the same size, as given by their atomic volumes. Fluorine, chlorine, or hydroxyl may replace (or "proxy" for) oxygen rather than hydrogen; potassium does not "proxy" for hydrogen, nor titanium for silicon. Calculations from the best published analyses of biotites show a range in the atomic percentages (omitting O, H, F) : Si 31·8 to 38·5 (*i.e.*, 5/16 to 6/16), Al 12·7 to 25 (*i.e.*, 2/16 to 4/16), Mg + Fe^{II} + Mn 16·5 to 36·8 (*i.e.*, 3/16 to 6/16), and K (+ Na + Ba + Ca) near 12·5 (2/16). The series therefore ranges from $H_4K_2Mg_6Al_2Si_6O_{24}$ (phlogopite) to $H_4K_2Mg_5Al_4Si_5O_{24}$ (eastonite), with the corresponding iron compounds $H_4K_2Fe_6Al_2Si_6O_{24}$ (annite) and $H_4K_2Fe_5Al_4Si_5O_{24}$ (siderophyllite). Here titanium and ferric iron "proxy" for magnesium, and not for silicon and aluminium. The several analyses are plotted on a square diagram at the four corners of which are the above hypothetical compounds. The optical constants plotted on the same diagram show some relations with the chemical composition. In the above formulæ the fundamental unit has in all cases 16 atoms (H and O being omitted), and these micas are therefore referred to the "octophyllite" or biotite system. In another group of micas, the "heptaphyllite" or muscovite–lepidolite system, there are 14 atoms in the fundamental unit. Here there are four end-members : $H_4K_2Al_6Si_6O_{25}$ (muscovite), $H_4K_2Li_6Si_6O_{18}$ (polylithionite), $H_4K_2Al_4Si_8O_{45}$ (phengite), and $H_4K_2Fe^{II}{}_3Al_4Si_5O_{22}$ (protolithionite), which are placed at the corners of a tetrahedron. The majority of plotted analyses fall on or near two of the surfaces of

[21] *Amer. J. Sci.*, 1925, [v], **9**, 309, 415; *A.*, ii, 592.

the tetrahedron, and are representative of two three-component systems, muscovite–polylithionite–protolithionite and muscovite–protolithionite–phengite, which are referred to as the muscovite and lepidolite systems, respectively. The optical data of these micas are represented by contour lines on the same tetrahedron. The octophyllites and the heptaphyllites are the two main groups of the micas between which there are no mixed crystals; the former are usually dark-coloured and the latter are usually light-coloured, and there are important differences in their optical characters.

This idea of "volume isomorphism" in the silicates had been previously considered by F. Zambonini [22] and by E. T. Wherry [23] in connexion with the well-known case of albite ($NaAlSi_3O_8$) and anorthite ($CaAl_2Si_2O_8$)—this pair forming a complete series of mixed crystals in the plagioclase felspars. Here NaSi and CaAl are evidently the replacing pairs. The sum of their atomic volumes [24] as calculated from W. L. Bragg's (1920) atomic radii are approximately the same, and the two atoms taken together will fit into the same crystalline structure. Further, it is to be noticed that the sum of the valencies of the two pairs of replacing atoms is the same. A similar case is given by the isomorphism of diopside ($CaMgSi_2O_6$) and acmite ($NaFe^{III}Si_2O_6$), and also by calcite ($CaCO_3$) and sodium nitrate ($NaNO_3$). This, however, seems to be only a re-statement of the fact pointed out by J. D. Dana as long ago as 1850 that the molecular volumes (molecular weight/density) are approximately equal for these pairs of isomorphous substances.

The same replacement of NaSi by CaAl as in the plagioclases is also worked out by A. N. Winchell [25] for the several minerals of the zeolite group. For example, the published analyses of thomsonite are plotted on a square at the four corners of which are the lime and soda molecules $Ca_3Al_6Si_{10}O_{32},Aq$, $Na_6Al_6Si_{10}O_{32},Aq$, $Ca_5Al_{10}Si_6O_{32},Aq$ and $Na_{10}Al_{10}Si_6O_{32},Aq$, the varying ratios $Al_2O_3 : SiO_2$ and $CaO : Na_2O$ being shown along the two co-ordinates. The analyses fall along a curved line between the points $Na_4Ca_8Al_{20}Si_{20}O_{80},25H_2O$ and $Na_7Ca_5Al_{17}Si_{23}O_{80},20H_2O$, which are regarded as the end-members of an isomorphous series. Quite different results have been arrived at for thomsonite by other authors. E. T. Wherry,[26] by plotting Na_2O against SiO_2, obtains two well-marked clusters: one around the composition $NaCa_2Al_5Si_5O_{20},6H_2O$, corresponding with thom-

[22] *Atti (Rend.) R. Accad. Lincei*, 1922, [v], **31**, (i), 295; *Amer. Min.*, 1923, **8**, 81.

[23] *Amer. Min.*, 1922, **7**, 113.

[24] E. T. Wherry, *ibid.*, 1923, **8**, 1, calculates the atomic volumes: O = 1, H = 5, Si = 7, Al = 11, Ca = 22, Na = 23×10^{-24} c.c.

[25] *Ibid.*, 1925, **10**, 88, 112, 145, 166.

[26] *Ibid.*, 1923, **8**, 121; 1925, **10**, 342.

sonite proper; and the other around $Na_2Ca_3Al_8Si_9O_{34},9H_2O$, corresponding with faroelite. Each of these minerals possesses definite optical constants, and there is no range of variation, as would be the case in an isomorphous series. Deviations shown by some analyses are ascribed to mechanical mixtures with natrolite or mesolite. From the same series of published analyses S. G. Gordon[27] calculates the molecular ratios with $Na_2O = 1$; CaO then ranges from 1·00 to 5·97. When the total $Na_2O + CaO$ is plotted against SiO_2 and against H_2O the analyses are grouped along straight lines, which indicate the isomorphous mixing of the end-members

$CaAl_2Si_2O_8,3H_2O$ (" calciothomsonite ")

and $Na_2Al_2Si_3O_{10},H_2O$.

In other groups a similar wide diversity of opinion is also shown in recent papers. The melilite group was the subject of much experimental work at the Geophysical Laboratory in Washington.[28] B. Gossner,[29] however, regards as improbable the existence of such complex molecules and he traces a connexion between these tetragonal minerals and the monoclinic (" pseudo-tetragonal ") pyroxenes. They are regarded as double compounds $CaO +$ pyroxene of the form $CaO,[SiO_3Ca,SiO_3Mg]$, where SiO_3Mg is replaceable by Al_2O_3, and Si_2O_6MgCa by Si_2O_6AlNa. Gehlenite is written

$CaO,[SiO_3Ca,Al_2O_3]$,

and melilite as $2CaO,[Si_2O_6MgCa,Si_2O_6AlNa]$. A. N. Winchell,[30] on the other hand, regards the molecules $Ca_2Al_2SiO_7$ (gehlenite) and $Ca_2MgSi_2O_7$ (åkermanite) as well-established end-members of the group; but the hypothetical molecule $Ca_3Al_2Si_3O_{12}$ or

$(9Ca,Na_2)_3Al_2Si_3O_{12}$

(sarcolite) he thinks is doubtful. The last may be split up into $Ca_2Al_2SiO_7$, $Ca_3Si_2O_7$, and SiO_2. Including Si with R, these, as well as gehlenite and åkermanite, reduce to the general type R_5O_7; and they are therefore regarded as replaceable in the space-lattice of melilite. The excess of silica is supposed to fall into the interatomic spaces, thereby producing a considerable effect on the density, but little effect on the refractive indices.

Correlations of the optical constants with the chemical composition in isomorphous groups of minerals have been shown graphically on plots of various kinds by several authors, especially by A. N. Winchell[31] in a series of papers on the pyroxenes, amphiboles, scapolites, and micas. Accurately determined data, all determined

[27] *Proc. Acad. Nat. Sci. Philadelphia*, 1924, **76**, 103; *A.*, 1924, ii, 868.
[28] *Ann. Report*, 1920, **17**, 213; 1923, **20**, 268.
[29] *Chemie der Erde*, 1925, **2**, 103; *A.*, ii, 821.
[30] *Amer. J. Sci.*, 1924, [v], **8**, 375; *A.*, ii, 152.
[31] *Ibid.*, 1923, [v], **6**, 504; 1924, **7**, 287; 1925, **9**, 309, 415; *Amer. Min.*, 1924, **9**, 108; 1925, **10**, 335.

on the same sample of material, and thus suitable for purposes of correlation, have been given by H. S. Washington and H. E. Merwin,[32] and by N. Sundius [33] for various pyroxenes and amphiboles. Unfortunately, with many recent mineral analyses the authors omit to state the density of the material analysed. Many published mineral analyses have been made solely for purposes of identification, and these should not be taken into account when attempting to arrive at the constitution of minerals.

The chemical composition of isomorphous groups of silicates (tourmaline, chlorite, mica) were studied by E. S. Fedorov [34] by graphically plotting the analyses. With three or four independent variables, different methods of plotting involving a special geometry were devised. The composition of various silicate minerals is represented by points on or in a " chemical tetrahedron," and the positions of these points are expressed geometrically by symbols resembling crystallographic indices. At the four corners of the tetrahedron are grouped the univalent, bivalent, tervalent, and quadrivalent elements, respectively [35] (oxygen being omitted). The symbol for quartz will then be (0001), for corundum (also hæmatite) (0010), spinel (0120), albite (1013), anorthite (0122), etc. The three main types of micas are (1011), (0445), and (4403), corresponding respectively with muscovite, biotite, and phlogopite. These points are all on the surface of the tetrahedron. Points representing the more complex chlorites fall inside the tetrahedron, and all in a plane with the indices ($\bar{6}$456). Amesite,

$$H_4(Mg,Fe)_2Al_2SiO_9$$

or (4221), shows the relation $\bar{6} \times 4 + 4 \times 2 + 5 \times 2 + 6 \times 1 = 0$; and the same holds with the other chlorites, clinochlore (8523), delessite (5222), corundophyllite (20·11·8·6), etc.

The System Alumina–Silica.

The trimorphous minerals andalusite, fibrolite, and kyanite, with the composition Al_2SiO_5 or Al_2O_3,SiO_2, are well known, and in certain rocks they are of abundant occurrence in nature. Kyanite is typically a product of the dynamic (or pressure) metamorphism of rocks, whilst andalusite and fibrolite are often the products of contact (or thermal) metamorphism. Neither andalusite nor kyanite has been prepared artificially; and it is now said that the supposed artificial fibrolite is not Al_2O_3,SiO_2, but $3Al_2O_3,2SiO_2$.

[32] *Amer. Min.*, 1923, **8**, 63, 104, 215.

[33] *Geol. För. Förh.*, 1924, **46**, 154.

[34] *Bull. Acad. Sci. Russie*, 1918, [vi], **12**, 615, 625, 645, 1891; [*Min. Mag.* (*Abstr.*), 1925, **2**, 425].

[35] Similar to Fig. 2 in *Ann. Report*, 1923, **20**, 267, but with univalent elements at one corner in place of MgO or CaO.

There is thus a recurrence of the once vexed question of the composition of fibrolite. In the old text-books on mineralogy bamlite, bucholzite, fibrolite, monrolite, sillimanite, wörthite, and xenolite have at one time or another ranked as distinct species. Analyses showed widely varying ratios of alumina to silica, due, as now known, to the intimate intermixture of silica with the finely fibrous and dense material (and the same is true of the artificial product). These minerals are now all united under the species fibrolite, and modern text-books are all agreed on the formula Al_2O_3,SiO_2, although not on the mineralogical name to be applied to the species. The name Faserkiesel dates from 1792 and its equivalent fibrolite from 1802; whilst the name sillimanite, now in common use in petrography, was first given by G. T. Bowen in 1824.

The system alumina–silica was studied experimentally in the Geophysical Laboratory at Washington in 1909,[36] and the conclusion then arrived at was that the only compound is Al_2SiO_5. The crystalline product was identified with fibrolite, the crystallographic and optical characters agreeing with those of the natural mineral (although it was noticed at the time that the crystals were mixed with glass and that they had refractive indices slightly lower than those of natural fibrolite).

Later work in the Geophysical Laboratory by N. L. Bowen[37] and his collaborators, in 1924, showed that this artificial product, eliminating the glass, has the composition $3Al_2O_3,2SiO_2$. And it is further asserted that all " fibrolite " previously prepared artificially has the same composition. A mixture of alumina and silica in equal molecular proportions was found to crystallise from fusion as a mixture of $3Al_2O_3,2SiO_2$ and cristobalite (SiO_2) or glass. Above 1810°, this breaks down into corundum (Al_2O_3) and liquid. It was also found that natural fibrolite, when heated at 1545°, breaks down to $3Al_2O_3,2SiO_2$ and a highly siliceous glass. This compound $3Al_2O_3,2SiO_2$ is also described by the same authors as a natural mineral under the name *mullite*. This was found as microscopic crystals, which had earlier been referred to fibrolite, in the buchites (inclusions of fused slaty rocks in igneous intrusions) from the Island of Mull in Scotland. None of the three minerals with the composition Al_2O_3,SiO_2 could be obtained artificially, and they are ignored in the equilibrium diagram of the system Al_2O_3–SiO_2; but in view of their abundant occurrence in nature, their existence can-

[36] E. S. Shepherd, G. A. Rankin, and F. E. Wright, *Amer. J. Sci.*, 1909, [iv], **28**, 293; *Ann. Report*, 1909, **6**, 202. G. A. Rankin and F. E. Wright, *ibid.*, 1915, **39**, 1; *Ann. Report*, 1915, **12**, 243.

[37] N. L. Bowen and J. W. Greig, *J. Amer. Ceramic Soc.*, 1924, **7**, 238; N. L. Bowen, J. W. Greig, and E. G. Zies, *J. Washington Acad. Sci.*, 1924, **14**, 183; *A.*, 1924, ii, 416.

not very well be denied. The conditions operating in nature are evidently very different from those in the laboratory and in the study.

No essential difference is shown between the crystallographic and physical characters of fibrolite and mullite. Both are orthorhombic with the same prism angle and the highly perfect cleavage parallel to the brachy-pinakoid. The optical orientation is the same for both, and also the wide difference between the birefringences $\gamma-\alpha$ and $\beta-\alpha$ on the planes (010) and (001), respectively. They also give identical spectra by the *X*-ray powder method.[38] The only difference is that the refractive indices of mullite (α 1·642, γ 1·654) are slightly lower than those of fibrolite (α 1·657, γ 1·677). When, however, the crystals of mullite contain small amounts of impurities (Fe_2O_3 and TiO_2) the values, α 1·661 and γ 1·682, actually exceed those for fibrolite.

We have here a very unusual case showing an anomalous relation between chemical composition and crystalline structure. Crystals in which there are isomorphous replacements are expected to be very similar in their geometrical and physical properties; but here we have identity of properties with a different molecular ratio of $Al_2O_3 : SiO_2$. No similar case can be called to mind. Malachite [$CuCO_3$,$Cu(OH)_2$] and chessylite [$2CuCO_3$,$Cu(OH)_2$], though both monoclinic, are very different in structure and all their properties; matlockite ($PbCl_2$,PbO) and mendipite ($PbCl_2$,2PbO) are tetragonal and orthorhombic, respectively; alamosite (PbO,SiO_2) and barysilite ($3PbO,2SiO_2$), monoclinic and hexagonal; and many other similar examples could be cited. It would seem that some mistake has been made. The existence of fibrolite (Al_2O_3,SiO_2) cannot be denied.[39] If the existence of mullite as $3Al_2O_3,2SiO_2$ is confirmed, the suggestion may be made that the physical characters assigned to it are really those of fibrolite. Many examples can be collected from the literature of cases in which the chemical composition has been determined on material of one kind, whilst the crystallographic properties have been determined on material of another kind.[40] Difficulties of this kind are frequently met with when dealing with finely crystallised mixtures.

The artificial reproduction of fibrolite or mullite is of mineralogical and chemical interest, but it is also of considerable economic importance in the manufacture of refractory materials and ceramic ware.

[38] This is confirmed by F. Rinne, *Z. Krist.*, 1925, **61**, 113.

[39] Crystals of fibrolite from which excellent gems have been cut have recently been described (*Min. Mag.*, 1920, **19**, 107).

[40] For example, the characters of the so-called orthorhombic or β-tin, as quoted in the text-books, were determined on orthorhombic crystals of stannous sulphide (*Min. Mag.*, 1921, **19**, 113).

It has been prepared on a large scale in a crystalline form by smelting aluminous rocks or minerals with coke in a cupola furnace.[41] A review of the literature on the presence and development of artificial "sillimanite" in ceramic ware has been given by A. B. Peck.[42] He also describes an occurrence of andalusite-rock in California, which is mined with an output of about 70 tons per week, the material being used in the manufacture of the porcelain cores of sparking plugs for automobiles. This mineral when heated at about 1390° is transformed into a parallel aggregate of fibres of mullite with interstitial glass, the density changing from 3·29 to 3·20. Since the volume change accompanying this transformation is only slight, the powdered mineral can be mixed with the clay body before firing. Kyanite is transformed at about 1370° into an irregular interlocking aggregate of mullite fibres with interstitial glass, there being here a greater change in volume (*d* 3·59 to 3·09). J. W. Greig [43] finds that this decomposition takes place at no definite temperatures, but is lowest for kyanite and highest for fibrolite. Above 1050°, only mullite is stable. The decomposition of kyanite and of andalusite is accompanied by an absorption of heat.

The stability relations of the three minerals andalusite, fibrolite, and kyanite have been studied by F. Neumann.[44] The specific heat and heat of solution (in 40% hydrofluoric acid) were determined for each, and also for the mixture of mullite and silica prepared from equal molecular proportions of alumina and silica. These data are applied in Nernst's heat theorem, and from the "*A–U*" (work–energy) diagram for the pair andalusite–fibrolite, it is concluded that fibrolite is the stable modification up to 1487°, and that andalusite is stable above this temperature. Kyanite as compared with fibrolite is completely unstable. Direct experiments show, however, that when heated at 1200° andalusite changes into mullite and glass; and kyanite shows the same change at 1400°.

Colour in Minerals.

Minerals that possess no colour of their own may, when well developed as single crystals, be perfectly colourless, clear, and transparent. Examples are the rock-crystal variety of quartz and the Iceland-spar variety of calcite. Often, however, the crystals are cloudy or opaque, due to inclusions of foreign matter. If this foreign matter consists of ferric hydroxide, the crystal may be

[41] A. Malinovsky, *J. Amer. Ceram. Soc.*, 1920, **3**, 40; *Trans. Ceram. Soc.*, 1920, **19**, 140.

[42] *Amer. Min.*, 1924, **9**, 123; 1925, **10**, 253; *J. Amer. Ceram. Soc.*, 1925, **8**, 407.

[43] *J. Amer. Ceram. Soc.*, 1925, **8**, 465; *A.*, ii, 987.

[44] *Z. anorg. Chem.*, 1925, **145**, 193; *A.*, ii, 849.

yellow, brown, or red, as often seen in quartz and calcite. Or again, crystal aggregates may be intermixed with impurities of various kinds, as in the multi-coloured jaspers and marbles. In such cases the cause of the colour is obvious and is shown by an ordinary chemical analysis. In other cases the crystal, though brightly coloured, may still be perfectly clear and transparent: for example, the amethyst, cairngorm, and citrine varieties of quartz, which are used as gem-stones; wine-yellow and violet calcite; brilliant sky-blue halite (rock-salt); and fluorite with its wide range of delicate colours. The colour of emerald and ruby has been attributed to traces of chromium (and in the artificial gem-rubies the colour is produced by the addition of chromic oxide). But in the majority of cases chemical analysis gives no clue as to the cause of the colour. This " dilute colouring " is due, according to the theory of C. Doelter, to the presence of a colloidal substance, and the different colours to the degree of dispersity or size of the particles of the colloid. But it may be doubted if colloids can exist in a solid crystalline medium. Crystals of organic compounds are capable of taking up traces of aniline dyes, and it may be suggested that minerals are merely dyed with traces of inorganic (in some cases organic) colouring matter. Some colours are clearly due to the interference of light brought about by structures in the stone (as in mother-of-pearl); and it is evident that the colours of minerals cannot be all explained by any one theory. The main difficulty is presented by certain minerals that exhibit remarkable changes in colour with change in temperature and when exposed to radium emanations, ultra-violet rays, cathode-rays, *X*-rays; and further, these changes are often accompanied by striking luminescent and phosphorescent effects in the mineral. Such changes have been studied by C. Doelter and others, but with very erratic results, and the same effects cannot always be repeated.

The various colour-varieties of quartz have recently been investigated in detail by E. F. Holden.[45] The colour of citrine he attributes to sub-microscopic particles of ferric hydroxide. Deep-amber coloured material was found to contain 0·026% Fe_2O_3, whilst specimens with a pale yellowish tinge contained only 0·008% to 0·011%. Further, the darker colour was closely imitated with a colloidal solution of ferric hydroxide of the same degree of concentration, and the absorption-spectrum of light transmitted through this solution is identical with that of citrine. Pink crystals of quartz contained 0·043% Fe_2O_3 and showed microscopic inclusions of hæmatite. This colour was imitated by mixing finely powdered hæmatite with sodium silicate. Rose-quartz showed in 27 analyses

[45] *Amer. Min.*, 1923, **8**, 117; 1924, **9**, 75, 101; 1925, **10**, 127, 203; *A.*, 1924, ii, 620.

of material from various localities a loss on ignition of 0·10—0·25% and solid impurities 0·13—0·29%. Small amounts of MnO, TiO_2, Fe_2O_3, CoO, Li_2O, and Al_2O_3 were estimated. The manganese ranges with the depth of colour (pale pink to deep pink) from 0·0002 % to 0·0006% as MnO; and the conclusion is drawn that the colour is due to some manganic (Mn^{III}) compound. The absorption-spectrum and dichroism of rose-quartz are similar to those of substances known to contain Mn^{III}. Rose-quartz is decolorised at about 575°, and when exposed to radium it becomes smoky. Contrary to the statement in books on precious stones, the colour is not affected by sunlight.[46] The rose colour has been imitated in a silica gel by the addition of manganic borate (0·01—0·02% MnO). A rose-quartz with a bluish tinge contained 0·029% TiO_2 and showed under the microscope abundant inclusions of fine hairs of rutile, to which the bluish colour is ascribed. Smoky-quartz is immediately decolorised at 440° and slowly at 235°, and the colour is restored by radium radiations. The small amounts of iron, titanium, and manganese shown by analysis bear no relation to the depth of the colour; whilst uranium (UO_3 0·001—0·006%) and free silicon are most abundant in darker specimens. Free silicon was estimated by boiling the finely powdered mineral in aqua regia, when colloidal silicic acid passes into solution; the darker specimens gave Si 0·01%. The conclusion is drawn that the smoky colour is due to the scattering of light by atoms of free silicon and that these have been liberated by the action of radioactive substances. Amethyst is often associated with iron minerals and it frequently contains inclusions of goethite and hæmatite. It is decolorised at 26% and the violet colour is restored by radium. Darker-coloured specimens become yellow when ignited and then show the same absorption-spectrum as citrine. Manganese and titanium are present in only small amounts, which do not vary with the depth of colour. The average amounts of Fe_2O_3 in specimens free from visible inclusions range with the colour from 0·007% to 0·14%. The colour of amethyst is similar to that of ferric ammonium alum and is evidently due to some ferric compound, which when heated breaks down to ferric hydroxide.

The yellow and purple calcites from Joplin, Missouri, have been studied by W. P. Headdon[47] with special reference to the phosphorescent and luminescent phenomena which they display. When the mineral is heated at 250° for twenty minutes, many of these properties are destroyed and the colour is discharged. The pro-

[46] A richly coloured specimen of rose-quartz exhibited in the British Museum collection of minerals has been exposed to light since the year 1799.

[47] *Amer. J. Sci.*, 1923, [v], **5**, 314; 1923, **6**, 247; 1924, **8**, 509; *Proc. Colorado Sci. Soc.*, **1923**, **11**, 399; *A.*, ii, 561.

perties are again restored by exposing the calcite to radium, and the material then acquires a yellow colour. Some colourless and previously unresponsive calcites when exposed to radium acquire a yellow colour and become responsive. Detailed chemical analyses were made on large amounts of material (500 grams or even 25 lb.). A strongly phosphorescent, yellow calcite from Joplin contained, in addition to $CaCO_3$, about 99·80%: cerium earths 0·019, yttrium earths, 0·013, MgO 0·113, FeO 0·046, MnO 0·045, ZnO 0·014%. The purple Joplin calcite gave: cerium earths 0·0397, yttrium earths 0·0149, MgO 0·0949, Al_2O_3 0·0076, FeO 0·0148, MnO 0·0477, ZnO 0·0048, CuO 0·0090%. The difference in colour cannot be explained by these impurities in the calcite. It has, however, been noticed that the purple calcite alone shows the absorption-spectrum of neodymium, and the suggestion has been made that this is the cause of the purple colour, though there is no direct evidence to support this view. A curious feature was noticed accidentally with a colourless calcite from Ingleside, Colorado. This is sometimes phosphorescent after exposure to sunlight, but only after it has been washed on the surface with dilute hydrochloric acid.[48]

A change in colour due to oxidation of ferrous iron has been observed by A. Johnsen.[49] Pale yellow to green crystals of sphene from the Alps when heated to redness in air for half an hour become deep reddish-brown, and they then show a different pleochroism and a slight difference in the optic axial angle. When again heated in hydrogen, the original colour is very nearly restored. Material that contained before heating FeO 0·48, Fe_2O_3 0·04%, gave after heating in air FeO 0·40, Fe_2O_3 0·13%, and after subsequent heating in hydrogen FeO 0·52, Fe_2O_3 0·03%. These changes are taken to indicate that there has been a diffusion of material in the solid.

A somewhat similar case is shown by the mineral chlorophæite, though here the change in colour due to oxidation takes place spontaneously on exposure to air. This mineral, which occurs as patches in dolerite near Edinburgh, is pale olive-green with glassy lustre on freshly fractured surfaces. On exposure, the colour changes to dark green in about fifteen minutes, and after ninety minutes it is black with pitchy lustre. It was found that this change takes place also in the dark when the mineral is exposed to air; but not in an atmosphere of carbon dioxide, even on exposure to bright sunlight. The change is therefore due to oxidation, and not to the action of light. The change from pale green to black can be induced artificially by heating a fragment of the mineral in the oxidising part of a Bunsen-

[48] *Amer. J. Sci.*, 1924, [v], **8**, 509; *A.*, ii, 89.
[49] *Jahrb. Min. Beil.-Bd.*, 1923, **48**, 136.

flame. Analysis of the fresh mineral shows the presence of Fe_2O_3 12·37, FeO 9·18%.[50]

A fugitive colour in sodalite is described from Dungannon in Ontario.[51] A rock, consisting of nepheline, cancrinite, and calcite, showed on freshly fractured surfaces bright pink spots, but in direct sunlight these vanished in ten to thirty seconds. When the specimens are placed in the dark, the colour gradually returns, though not to the same brilliancy. The material of the pink areas was identified as sodalite, but the analysis shows no constituent, beyond a trace of manganese, to account for the colour. This colour change is evidently due to the action of light, and no further explanation can be offered. It was first noticed a century ago in sodalite from Greenland,[52] and later in sodalite from India and in hackmanite from Russian Lapland.

The action of radium radiations on the colour of minerals has been studied by many workers, and a good account has recently been given by S. C. Lind and D. C. Bardwell.[53] The colour produced by exposure to radium chloride or bromide is afterwards dispelled by heat or by exposure to sunlight. The most marked effects are given by fluorite and kunzite. Fluorite of all colours becomes blue in 1—3 days; the material when afterwards heated to 70° gives a blue luminescence, and at 180° the colour is discharged. Kunzite, the lilac-coloured variety of spodumene, becomes first colourless and then emerald-green; and is afterwards very brightly thermoluminescent. Diamond becomes green only when exposed to α-radiation (not β- and γ-radiation through glass); this colour is apparently light-permanent, but is dispelled at 450°. A theory to account for these changes assumes that certain groups of electrons are displaced and their vibration frequencies modified.

New Minerals.

A list of 211 new mineral names (not necessarily new minerals) covering the period 1922—1925, but including also a few earlier names that had remained buried in the scattered literature, has recently appeared.[54] A selection of these not mentioned in previous Reports is given below. A further crop of radioactive minerals from the deposits of uranium ore in the Katanga district of the

[50] R. Campbell and J. W. Lunn, *Min. Mag.*, 1925, **20**, 435; *A.*, ii, 1093.

[51] T. L. Walker and A. L. Parsons, *Univ. Toronto Studies, Geol. Ser.*, 1925, No. 20, 5.

[52] F. Mohs, "Treatise on Mineralogy," translated by W. Haidinger, 1825, **2**, 227.

[53] *J. Franklin Inst.*, 1923, **196**, 375, 521; *Amer. Min.*, 1923, **8**, 171, 201; 1924, **9**, 35.

[54] L. J. Spencer, "Tenth list of new mineral names; with an index of authors." *Min. Mag.*, 1925, **20**, 444.

Belgian Congo includes the new names: droogmansite,[55] dumontite,[56] fourmarierite, and sklodowskite.[57]

Some of these names are rather uncouth and they do not seem to be well chosen for international use.[58] The international aspect of Science is of prime importance. An original paper is written in the language of one country, but it is more widely read in the sum of other countries.

A system of Latin binomials (as in botany and zoology) was in use a century ago for minerals, but this has long since been given up. Another method that has been tried without success is that of using purely chemical names. This is favoured by Groth in his "Chemische Krystallographie"; for example, he substitutes for hannayite the name Tetrahydrogendiammoniumtrimagnesiumtetraorthophosphat-Oktohydrat. But this does not completely define the mineral hannayite—there may be others of the same composition. Further, future analyses of hannayite may prove this composition to be incorrect—to the confusion of indexers. For such minerals as tourmaline even Groth does not attempt a chemical name. The system now in vogue, in spite of its confusion and faults, is the best yet devised. It certainly is a convenience to use such names as diamond and graphite for the crystalline modifications of carbon found in nature; and calcite and aragonite for those of calcium carbonate.

Afwillite,[59] hydrated calcium silicate, $3CaO,2SiO_2,3H_2O$, or $2H_2CaSiO_4,Ca(OH)_2$, found as a single, columnar aggregate of clear, colourless crystals in the Dutoitspan diamond mine at Kimberley, South Africa. The crystals are monoclinic and the mineral is quite distinct from the several hydrated calcium silicates previously known. It has an alkaline reaction and is slowly decomposed by water.

Bardolite,[60] a dark-green, chlorite-like mineral with the empirical formula $K_2O,5MgO,FeO,2Fe_2O_3,Al_2O_3,12SiO_2,21H_2O$, intermediate between biotite and chlorite in composition. It is of interest because of its occurrence as a primary constituent in an igneous rock, namely in diabase at Bardo in central Poland.

[55] H. Buttgenbach, "Minéralogie du Congo Belge." *Mém. Soc. R. Sci. Liége*, 1925, [iii], **13**.

[56] A. Schoep, *Compt. rend.*, 1924, **179**, 693; *A.*, ii, 64; *Bull. Soc. franç. Min.*, 1925, **48**, 77.

[57] A. Schoep, *Compt. rend.*, 1924, **179**, 413; *Bull. Soc. franç. Min.*, 1924, **47**, 162; *Bull. Soc. chim. Belg.*, 1924, **33**, 562; *A.*, 1924, ii, 868; 1925, ii, 235.

[58] L. J. Spencer, "International agreement in mineralogical and crystallographical nomenclature." *Min. Mag.*, 1925, **20**, 353.

[59] J. Parry and F. E. Wright, *Min. Mag.*, 1925, **20**, 277; *A.*, ii, 429.

[60] J. Morozewicz, *Bull. Soc. franç. Min.*, 1924, **47**, 49; *Spraw. Polsk. Inst. Geol.*, 1924, **2**, 217; 1925, **3**, 1.

Benjaminite,[61] sulphobismuthite of lead, silver, and copper, $Pb_2(Ag,Cu)_2Bi_4S_9$, belonging to the klaprotholite group, and found as grey masses in white quartz from Nevada.

Bromellite,[62] beryllium oxide, BeO, found as small, white, hexagonal prisms in the iron mines at Långban in Sweden. It is very hard, about 9 on the scale. *X*-Ray analysis shows the crystal-structure to be of the zinc oxide type.

Cannizzarite,[63] a sulphobismuthite of lead, $PbS,2Bi_2S_3$, of recent formation as a sublimate in fumaroles on Vulcano, Lipari Islands. The acicular crystals appear to be orthorhombic.

Chapmanite,[64] hydrated ferrous silico-antimonate,

$$5FeO,5SiO_2,Sb_2O_5,2H_2O,$$

occurring as an olive-green, pulverulent material (probably orthorhombic) intermixed with native silver in the Keeley mine, South Lorrain, Ontario.

Foshagite,[65] hydrated calcium silicate, $5CaO,3SiO_2,3H_2O$ or $H_2Ca_5(SiO_4)_3,2H_2O$, as a white fibrous (orthorhombic) mineral filling veins in idocrase at Crestmore, California.

Fourmarierite, a hydrated uranium lead mineral occurring as minute, red, orthorhombic crystals intimately associated with kasolite, curite, and torbernite in the oxidised uranium ore of Kasolo, Katanga, Belgian Congo. H. Buttgenbach,[66] by whom the name was given, found also some silica, but this may belong to the associated kasolite. Analyses by J. Mélon [67] on material separated as far as possible from other minerals suggested the formula $PbO,5UO_3,10H_2O$; while one by A. Schoep[68] gave $PbO,4UO_3,5H_2O$, which, written in the form $(UO_2,Pb)O,H_2O$, suggests a relation to becquerelite and schoepite.

Chlorophoenicite,[69] basic arsenate of manganese and zinc with small amounts of calcium, magnesium, and iron, with the highly basic formula $R_3As_2O_8,7R(OH)_2$. It is found at Franklin Furnace,

[61] E. V. Shannon, *Proc. U.S. Nat. Museum*, 1924, **65**, art. 24; *A.*, 1924, ii, 560. For other sulphobismuthites of lead see Cannizzarite and Goongarrite below; still others have been described by K. Johansson, *Arkiv Kemi, Min. Geol.*, 1924, **9**, no. 8.

[62] G. Aminoff, *Z. Krist.*, 1925, **62**, 113.

[63] F. Zambonini, O. de Fiore, and G. Carobbi, *Rend. Accad. Sci. Fis. Mat. Napoli*, 1925, [iii], **31**, 24; *A.*, ii, 709.

[64] T. L. Walker, *Univ. Toronto Studies, Geol. Ser.*, 1924, No. 17, 5.

[65] A. S. Eakle, *Amer. Min.*, 1925, **10**, 97.

[66] *Ann. Soc. Géol. Belg.* (*Publ. Congo Belge*), 1924, **47** (for 1923–4), C 41.

[67] *Ann. Soc. Géol. Belg.* (*Bull.*), 1925, **47**, B 200.

[68] *Bull. Soc. franç. Min.*, 1924, **47**, 157; *Bull. Soc. chim. Belg.*, 1924, **33**, 558; *A.*, 1925, ii, 236.

[69] W. F. Foshag and R. B. Gage, *J. Washington Acad. Sci.*, 1924, **14**, 362; *A.*, 1924, ii, 773.

New Jersey, as small, monoclinic prisms, which are pale green by daylight and pale purplish-red in artificial light (hence the name).

Elatolite,[70] a form of calcium carbonate believed to represent the high-temperature α-form stable above 970°. It is represented by cavities with the form of fir-trees (ἐλάτη) in the nepheline-syenites of the Kola peninsula in Russian Lapland. The dendritic crystals that have been leached out of these cavities were evidently an original constituent of the igneous rock.

Ellsworthite,[71] hydrated metatitano-niobate of uranium (UO_3 18·5%), calcium, and iron, $RO,Nb_2O_5,2H_2O$, occurring as yellow or brown, optically-isotropic masses in pegmatite at Hybla, Ontario. In its degree of hydration it is intermediate between hatchettolite and ampangabeite.

Goongarrite,[72] a sulphobismuthite of lead, $4PbS,Bi_2S_3$, occurring as fibrous to platy (monoclinic ?) masses in a gold-quartz vein near Lake Goongarrie, Western Australia.

Kempite,[73] hydrated oxychloride of manganese,

$$MnCl_2,3MnO_2,3H_2O,$$

as small, emerald-green, orthorhombic crystals in manganese ore from California.

Kochite,[74] hydrated aluminium silicate, $2Al_2O_3,3SiO_2,5H_2O$, as a granular aggregate of minute, cubic crystals at Kochi-mura, Japan.

Manganolangbeinite,[75] manganese and potassium sulphate, $2MnSO_4,K_2SO_4$, as minute, pale-rose tetrahedra from Vesuvius. It is analogous to the cubic double salt langbeinite, $[2MgSO_4,K_2SO_4]$.

Mullite, orthorhombic, $3Al_2O_3,2SiO_2$ (*see* p. 269).

Ramsayite,[76] sodium titanosilicate, $Na_2O,2SiO_2,2TiO_2$, occurring as brown, orthorhombic crystals resembling sphene in nepheline-syenite-pegmatite in the Kola peninsula, Russian Lapland.

Schallerite,[77] hydrated arseno-silicate of manganese,

$$9MnSiO_3,Mn_3As_2O_8,7H_2O,$$

as pale-brown masses filling veinlets in zinc ore at Franklin Furnace, New Jersey. It has a pearly basal cleavage and is optically uniaxial, and is analogous to friedelite $[9MnSiO_3,MnCl_2,7H_2O]$.

[70] A. E. Fersman, *C. R. Acad. Sci. Russie*, 1922, 59; *Bull. Acad. Sci. Russie*, 1923, [vi], **17**, 251.

[71] T. L. Walker and A. L. Parsons, *Univ. Toronto Studies, Geol. Ser.*, 1923, No. 16, 13.

[72] E. S. Simpson, *J. Roy. Soc. Western Australia*, 1924, **20**, 65.

[73] A. F. Rogers, *Amer. J. Sci.*, 1924, [v], **8**, 145; *A.*, 1924, ii, 693.

[74] S. Kôzu, K. Seto, and K. Kinoshita, *J. Geol. Soc. Tokyo*, 1922, **29**, 1, 148; *Sci. Rep. Tôhoku Univ.*, 1924, [iii], **2**, 1.

[75] F. Zambonini and G. Carobbi, *Rend. Accad. Sci. Fis. Mat. Napoli*, 1924, [iii], **30**, 123; *A.*, 1924, ii, 867; *Gazzetta*, 1925, **55**, 414; *A.*, ii, 898.

[76] A. E. Fersman, *C. R. Acad. Sci. Russie*, 1922, 59; E. E. Kostyleva, *ibid.*, 1923, 55.

[77] R. B. Gage, E. S. Larsen, and H. E. Vassar, *Amer. Min.*, 1925, **10**, 9.

Swedenborgite,[78] antimonate of aluminium and sodium, $NaAl_2SbO_6$, as colourless, hexagonal crystals from Långban, Sweden.

Wenzelite,[79] hydrated phosphate of manganese, etc.,

$$(Mn,Fe,Mg)_3(PO_4)_2,5H_2O,$$

as rosettes of pale rose-red, monoclinic crystals from the phosphate-bearing pegmatites at Hagendorf, Bavaria. Similar crystals, also rose-red and monoclinic from the same locality, but with the composition $R_3(PO_4)_2,3H_2O$, have been called baldaufite.[80]

New Books.

"A chart showing the chemical relationships in the mineral kingdom" has been prepared by P. C. Putnam (J. Wiley & Sons, New York; Chapman & Hall, London, 1925). This will be found useful to chemists as well as to mineralogists. It gives the answer to such questions as: "How many and what are the minerals containing germanium, and what are their compositions?"; "Does silver occur with oxygen in any mineral?"; or "Do phosphides or silicides occur as minerals?" It serves as an aid to determinative mineralogy and the microchemical analysis of minerals. And, further, gives at a glance a statistical survey of the affinities and the antipathies that hold in the mineral kingdom. The chart is printed on a sheet measuring a yard across and is mounted on linen. Along the edges various chemical elements, acid radicals, etc., are listed, there being 93 and 54 such entries in the two directions. Ruling vertical and horizontal lines, 5022 "boxes" are thus provided, in which practically all known minerals are placed. A mineral of complex composition will of course appear in several "boxes." The minerals are referred to by numbers 1—1632; and alphabetical and numerical indexes are given in the text. It is thus possible to see at a glance what minerals contain, say, both lead and sulphur, lead and uranium, lead and aluminium, etc. The idea is a good one and the chart will serve many useful purposes.

A new edition has appeared of P. Niggli's "Lehrbuch der Mineralogie." The first volume (Borntraeger, Berlin, 1924) is really a treatise on crystallography, but two more volumes dealing with special mineralogy and mineral associations ("Minerocoenology") are to follow. The treatment is fresh, and the book is full of novel and brilliant ideas, giving stimulus to research. H. Buttgenbach's "Les minéraux et les roches," a general and elementary text-book, has reached a third edition (Dunod, Paris; H. Vaillant-Carmanne, Liége, 1924). A fifth edition of the late H. Rosenbusch's well-

[78] G. Aminoff, *Z. Krist.*, 1924, **60**, 262.

[79] F. Müllbauer, *ibid.*, 1925, **61**, 333. In the original paper the name is given erroneously as Wentzelit, after Pater Hieronymus Wenzel.

[80] F. Müllbauer, *loc. cit.*, 334.

known "Mikroskopische Physiographie der Mineralien und Gesteine" is in preparation. The first half of vol. I (1921—4) has been revised by E. A. Wülfing and deals with the methods of investigation, involving crystal-optics, separation of minerals, microchemical tests applicable to powdered minerals and to thin sections, etc. The second half by O. Mügge gives a systematic description of the rock-forming minerals. In the first part so far issued (1925) the minerals of the cubic, tetragonal, hexagonal (and trigonal) systems are dealt with.

W. Eitel in "Physikalisch-chemische Mineralogie und Petrologie" (T. Steinkopff, Dresden and Leipzig, 1925) gives a condensed report on the work done during the past ten years on the many physical-chemical problems bearing on the formation and equilibrium of minerals and rocks. Numerous references are given to the original literature and there is a long index of authors. The same author in his prize essay "Über die Synthese der Feldspatvertreter" (Akad. Verlagsgesell., Leipzig, 1925) gives a detailed review of the literature on the synthesis of the felspathoid minerals (leucite, nepheline, gehlenite, melilite, sodalite, cancrinite, scapolite, etc.), with a discussion and equilibrium diagrams of the various systems in which they have been obtained artificially by fusion. An account is also given of his own work on carbonate–silicate fusions. The bearing of these experiments on the paragenesis of these minerals in natural rocks is considered.

A pamphlet [81] on "The physical chemistry of igneous rock formation" contains a series of ten papers by various authors, which were presented for general discussion at a joint meeting of the Faraday, Geological, and Mineralogical Societies in London. Contributed remarks and the discussion that arose are also included.

L. J. Spencer.

[81] Reprinted from *Trans. Faraday Soc.*, 1925, **20**, 413.

COLLOID CHEMISTRY.*

The development of colloid chemistry has been reviewed by W. D. Bancroft,[1] and a series of classical papers has been translated and edited by E. Hatschek.[2] A nomenclature and system for colloid chemistry suggested by P. D. Zacharias[3] would substitute the term metachemistry in place of colloid-, capillary-, or dispersoid-chemistry, so that one would be free from dogmatic restraint and able to use freely chemical and physicochemical methods. Solutions would be divided into three classes based on the size of the particles in solution. What are now termed colloid particles become "Teilchen" (Gk. $\tau\acute{\iota}\lambda\eta$), these being elementary, compound, and complex. The author's paper is decidedly heterodox in places. A. Lumière[4] believes that there are two colloidal states of matter, the molecular colloidal state and the micellary colloidal state, the classification being based on the structure of colloids, not on their properties. In the first state the solute is dispersed in a solvent as individual molecules but of high molecular weight, colloidality being a consequence. The properties depend on the dimensions and chemical functions of the molecules. The second state deals with pseudo-solutions, stabilisation factors being prominent, and the properties depend on the constitution of the molecular aggregates, the nature and importance of impurities, and the electric charge.

Another classification into two groups is suggested by L. Michaelis and Sh. Dokan.[5] They are obligative colloids (which cannot exist in true solution, *e.g.*, mastic) and facultative colloids (which consist of suspensions of a solid, *e.g.*, silver iodide, in its saturated solution). In the case of obligate colloids, hydrogen- and hydroxyl-ions hold a special place amongst ions in respect to their influence on electric charge and consequently on the effect on general properties.

* This Report has been prepared on behalf of the British Association Committee on Colloid Chemistry (Prof. F. G. Donnan, Chairman; Dr. Wm. Clayton, Secretary; Prof. J. W. McBain, Mr. E. Hatschek, Prof. W. C. McC. Lewis) by the Secretary.

[1] *J. Franklin Inst.*, 1925, **199**, 727.

[2] "Foundations of Colloid Chemistry" (London, 1925).

[3] *Kolloid-Z.*, 1925, **36**, 39; *A.*, ii, 196.

[4] *Rev. gén. Coll.*, 1925, **3**, 161.

[5] *Kolloid-Z.*, 1925, **37**, 67; *A.*, ii, 963.

Facultative colloids are influenced by electrolytes in general, and results in this connexion are given relating to colloidal barium sulphate.

J. Alexander [6] extends his previous work on the zone of colloidality by a short paper on the "Simple Kinetic Principle of Colloid Processes," dealing with the behaviour of heated iron and steel to illustrate the general principle that maximum colloidality follows when both the specific surface and the kinetic activity reach medium values.

Several contributions have been made by P. P. von Weimarn. In an extensive paper [7] he reviews his work of several years under the title "The Precipitation Laws." His four laws governing the precipitation of solid substances from solution are given :

Law I. The mean magnitude of the individual crystals of precipitates will progressively decrease as the concentration of the reacting solutions progressively increases.

Law II. With progressively increasing concentration of the reacting solutions, the mean magnitude of the individual crystals of precipitates (as determined after a definite time interval from the moment of mixing together the reacting solutions) will pass through a maximum.

Law III. For a set of dispersion media in which a solid substance, X, has different solubilities, the precipitation curves for that particular dispersion medium in which, other things being equal, the dispersion is least, will occupy the lowest position beneath all other precipitation curves, and their beginning will be displaced to the left.

Law IV. On substituting for the absolute concentration of the reacting solutions (C) the relative concentration of the precipitating substance, $(Q—L)/L$ (where $Q = C/2$, since equal volumes are mixed) the precipitation curves without maximum for the substance X precipitating from different dispersion media, where $L = L_1, L_2, L_3 \ldots L_n$, will very closely approach one another, up to the point of sometimes almost merging into a single curve.

Here $(Q—L)$ is the concentration of the dispersed phase produced, L being the normal solubility of this phase. The ordinate of the curves expresses the mean size of the crystals, and the abscissæ give the concentration of reacting solutions. The review is a valuable summary of von Weimarn's researches. Another summary [8] deals with his general views on the colloid state, whilst the influence of added substances on the permanence of disperse

[6] *Kolloid-Z.*, 1925, **36**, 334; *A.*, ii, 779.
[7] *Chemical Reviews*, 1925, **2**, 217.
[8] *Kolloid-Z.*, 1925, **36**, 237; *A.*, ii, 660.

systems receives theoretical treatment along lines familiar to students of von Weimarn's work.[9]

An interesting contribution from H. Siedentopf [10] deals with the proof of the form of ultramicrons. The mathematics and use are described of an apparatus which can be used to measure microscopic and ultramicroscopic dimensions, being based on the Michelson experiment on the interferometer measurement of fixed stars too small for the ordinary telescope.

H. R. Kruyt and H. C. Tendeloo [11] criticise the point of view taken by Loeb on the question of the significance of the hydrogen-ion concentration as a factor in determining the condition of lyophilic sols. They believe "the action of electrolytes on lyophilic colloids does not differ in essence from that on lyophobic colloids. The peculiar matter from which the particles of a protein are built up brings about that the H· and OH′ ions have quantitatively special function," but not an all-determining function. Loeb believed the isoelectric point to depend on a definite p_H value, but Kruyt and Tendeloo find that the isoelectric point can be reached at various p_H values by adding a quantity of another electrolyte just sufficient to produce discharge. Moreover, it is possible to pass through the isoelectric point as a minimum by means of ions other than H· or OH′. Emulsoid sols must be regarded as hydrated suspensoids, electric charge still being one of the stability factors. The authors consider that the essence of the problem of electric charge lies in the study of electrokinetic phenomena, these being observed in the whole region of colloids, lyophilic and lyophobic.

Another pertinent criticism of Loeb's work is given by W. Kopaczewski,[12] who believes that since the colloid state is an intermediate state defined by dispersion limits, its laws will be neither exclusively physical nor exclusively those of classical chemistry.

Sols.

The preparation and properties of some protected silver sols have been described by I. D. Garard and G. E. Duckers.[13] Alkaline silver nitrate solutions were reduced with formaldehyde or glucose, agar-agar, dextrin, and gum arabic being present as protective colloids. Gum arabic–silver sols were exceedingly stable against

[9] *Kolloid-Z.*, 1925, **37**, 151; *A.*, ii, 969.
[10] *Ibid.*, 1925, **36** (*Zsigmondy Festschr.*), 1; *A.*, ii, 637.
[11] *J. Physical Chem.*, 1925, **29**, 1303; *A.*, ii, 1059.
[12] "L'Etat Colloidal et L'Industrie" (Paris, 1925), Tome I, 40—50.
[13] *J. Amer. Chem. Soc.*, 1925, **47**, 692; *A.*, ii, 391.

the addition of various electrolytes over a wide range of concentration. According to V. Morávek,[14] stable silver sols may be prepared by reducing ammoniacal silver nitrate with chloroform in the presence of gelatin, heating at 90° for about 20 minutes. Continuing the study of the analysis and constitution of sols, E. Fried and W. Pauli [15] find that silver sols prepared by the reduction of ammoniacal silver chloride with hydrazine hydrate, contain ammonium ion. Experiments on dialysis, conductivity, cataphoretic mobility and addition of electrolytes are described. The condition of the silver in protargol and collargol (therapeutic sols) has been investigated by I. M. Kolthoff and O. Tomiček,[16] carrying out potentiometric titrations with iodine. Work closely related in scope and methods has been published by R. B. Smith and P. M. Giesy.[17]

Considerable attention has been given to silicic acid sols. W. Grundmann [18] shows that it is possible to prepare silicic acid sols of definite uniformity. Attention must be paid to the ratio of hydrochloric acid and sodium silicate used. The solution must be dialysed immediately in collodion membranes of standard thickness, using distilled water at a definite rate of flow. Contaminating vapours must be avoided. The sols are very stable and show very little light-dispersion.

By the addition of hydrochloric acid to sodium silicate solutions two types of silicic acid sol are possible.[19] 50 grams of sodium silicate in 200 c.c. of water + 70 c.c. of 20% acid gives a sol of p_H 4·5, whilst using only 150 c.c. of water gives a sol of p_H 6 or higher. The first sol shows a viscosity increasing with time; the second decreases with time owing to occluded silicate. The sols are negatively charged and stable at 20°. By adding hydrochloric acid to the second sol to reduce its p_H to about 4·5, sol I results; conversely, addition of caustic soda to sol I gives the second type.

The constitution and stability of silicic acid sols have been investigated by Wo. Pauli and E. Valkó.[20] Sols were prepared by Graham's method, by saponification of the methyl ester of silicic acid, and by decomposition of silicon tetrachloride. Graham's sol has a well-defined conductivity and the constitution of the particles may be expressed: $[x(SiO_2 + nH_2O)ySiO_3H] + yH^+$ (or yNa^+). Dialysis furnished a sol wherein the kations $H^\cdot$ and $Na^\cdot$ are inter-

[14] *Chem. Listy*, 1925, **19**, 195; *A.*, ii, 775.
[15] *Kolloid-Z.*, 1925, **36**, 138; *A.*, ii, 390.
[16] *Rec. trav. chim.*, 1925, **44**, 103.
[17] *J. Amer. Pharm. Assoc.*, 1925, **14**, 10.
[18] *Kolloid-Z.*, 1925, **36**, 328; *A.*, ii, 775.
[19] H. R. Kruyt and J. Postma, *Rec. trav. chim.*, 1925, **44**, 765; *A.*, ii, 861.
[20] *Kolloid-Z.*, 1925, **36** (*Zsigmondy Festschr.*), 334; *A.*, ii, 521.

changeable. Very concentrated and pure stable sols result from electro-dialysis of dilute sols. The number of neutral molecules associated with a unit charge varied between 320 and 1200.

By the oxidation of solutions of ferrous hydrogen carbonate by chlorine water or hypochlorous acid, ferric hydroxide sols are prepared.[21] Sols are also produced when ferrous hydrogen carbonate solutions are oxidised by air or hydrogen peroxide, provided sufficient ferric chloride is present as peptising agent.[22] A long paper by N. Kühnl and Wo. Pauli[23] discusses ferric oxide sols prepared by peptisation of precipitated ferric hydroxide by ferric chloride. The stability and constitution ("ionogenic character") form the main theme. The same authors[24] deal with the structure of (Al—Fe) oxide sols, or what they term hetero—or mixed—peptides. These are sols obtained by peptisation of precipitated aluminium hydroxide with ferric chloride, or of precipitated ferric hydroxide with aluminium chloride. Considerable discussion concerns the constitution of such sols, a mixed-crystal space lattice with Fe and Al being suggested for the sol particles, an idea to be tested by *X*-ray analysis.

Colloidal bismuth has been prepared by A. Gutbier and T. Kautter[25] by reducing with aqueous sodium hydrosulphite a solution of bismuth nitrate in aqueous glycerol, gum arabic being present as stabiliser. Dialysis and subsequent evaporation on the water-bath yields a black metallic residue containing up to 36% of bismuth. From 1 to 2% colloidal sulphur is also included. The product redissolves in water, the particles being negatively charged.

The colloid chemistry of bismuth and its compounds forms the subject of a detailed investigation in Wo. Ostwald's laboratory.[26] Various sols were prepared. The metal sol may be obtained by reduction of bismuth tartrate in feebly alkaline solution with sodium hydrosulphite, and the dark brown sol may contain up to 3·5 mg. of bismuth per 1 c.c. By the action of hydrogen sulphide on bismuth nitrate solutions containing gum arabic, sols of bismuth sulphide are possible. Using the following concentrations of gum arabic (in %) 0·1, 0·25, 0·5, 1·0, the maximum concentration of bismuth (in mg. per c.c.) was 0·5, 1, 7, 10, respectively. Colloidal bismuth sulphoiodide (BiSI) was prepared by the reaction between thioacetic acid and sodium bismuth iodide in the presence of gum

[21] G. Stadnikov and N. N. Gavrilov, *Kolloid-Z.*, 1925, **37**, 40; *A.*, ii, 861.
[22] N. N. Gavrilov, *ibid.*, p. 46; *A.*, ii, 860.
[23] *Koll. Chem. Beihefte*, 1925, **20**, 319; *A.*, ii, 776.
[24] *Ibid.*, p. 338; *A.*, ii, 776.
[25] *Z. anorg. Chem.*, 1925, **146**, 166; *A.*, ii, 860.
[26] A. Kuhn and H. Pirsch, *Koll. Chem. Beihefte*, 1925, **21**, 78.

arabic. With this sol many tests were made on the efficiency of such protective colloids as gum arabic, gelatin, and hæmoglobin. In another paper, Kuhn and Pirsch [27] deal with the peptisation of bismuth hydroxide and the action of glycerol and sugars as peptising agents. Sucrose and mannitol have optimum efficiency in 0·05*N*-solutions.

Colloidal sulphur has been prepared by P. P. von Weimarn and S. Utzino.[28] Pure rhombic sulphur (1 gram) is ground intensively with 0·9 gram of dextrose in an agate mortar; 0·15 gram is then energetically stirred into 100 c.c. of freshly-distilled water. The authors' sols contained between 30 ~ 20 mg. per litre, the mean particle size being 90 ~ 80 $\mu\mu$, the particles being negatively charged. The sols were stable for 5 to 10 days. The stability-period of the sols when treated with various electrolytes gave characteristic curves, stability in days being plotted as ordinates and electrolyte concentrations as abscissæ. Three groups follow from these curves : (1) curves with a maximum (NaCl, $CaCl_2$, $BaCl_2$, BaI_2, $CeCl_3$, HCl, H_2SO_4); (2) curves with two maxima (KCNS, $Ca[CNS]_2$); (3) curves with no maxima (KNO_3), *i.e.*, the stability is always lower than in the normal sol. The results are discussed on the assumption that adsorption and chemical force are identical in nature, differing but in degree.[29]

The electrosynthesis of six sulphide hydrosols has been effected by F. V. von Hahn,[30] using molybdenum-, antimony-, lead- and copper-glance, sphalerite and iron pyrites. The electro-methods were the cathodic charging (Muller, and Lucas and Le Blanc), luminous arc (Bredig), and oscillating discharge (Svedberg). For the first time has been found a critical temperature for the electrosynthesis of metal sols, since molybdenum-glance would not disperse below 53°.

Treatment of a solution of mercuric chloride with hydrogen sulphide or soluble sulphide gives a black sol of mercury sulphide, intermediate white and yellow double compounds forming. The influence of excess of either reagent on the condition of the sol produced has been studied by N. I. Morosow.[31]

The photochemical decomposition of arsenic hydride results in a sol of arsenic.[32] Bubbling arsine and hydrogen through water in quartz vessels irradiated by a quartz mercury-vapour lamp gives first a yellow sol, then red, blue, and bluish-violet sols, the last two

[27] *Kolloid-Z.*, 1925, **36** (*Zsigmondy Festschr.*), 310; *A.*, ii, 525.
[28] *Mem. Coll. Sci. Kyōtō Imp. Univ.*, 1925, *A*, **8**, 291.
[29] Compare *Kolloid-Z.*, 1913, **12**, 298.
[30] *Ibid.*, 1925, **36** (*Zsigmondy Festschr.*), 277; *A.*, ii, 522. [31] *Ibid.*, p. 21.
[32] L. Dede and T. Walther, *Ber.*, 1925, **58**, 99; *A.*, ii, 197.

unstable. The particles are negatively charged, and the red sols are very stable towards electrolytes.

Colloidal cobalt hydroxide has been prepared by C. Paal and H. Boeters [33] by alternately adding small amounts of aqueous cobalt chloride and sodium hydroxide to a solution of sodium protalbate or lysalbate. The resulting sol of cobaltous hydroxide oxidises during dialysis, especially if hydrogen peroxide is present, forming cobaltic hydroxide sol. Reduction of this solution by hydrogen in the presence of palladium slowly but completely results in a hydrosol of the metal.[34]

Hydrosols and gels of silver iodide have been described by A. Lottermoser, W. Seifert, and W. Forstmann,[35] the work being based on the conditions of titration of potassium iodide with silver nitrate.

By the reduction of potassium permanganate with sodium arsenite at 65—70°, sodium protalbinate being present, a stable brown sol of an oxide of manganese was prepared by A. Anargyros.[36] The sol rapidly liberates oxygen from hydrogen peroxide, especially in alkaline solution.

Several publications on the dispersion of cellulose in aqueous salt solutions are due to P. P. von Weimarn,[37] but his work is too voluminous to summarise here. The dispersion of clays is dealt with by G. Wiegner,[38] whose paper is useful for its theoretical survey of the charge on dispersed particles in relation to stability and flocculation.

Gold Sols.

Using methods previously described (*Kolloid-Z.*, 1923, **33**, 78) by von Weimarn for preparing gold hydrosols, special attention being given to dilutions and duration of heating, various stable sols are possible by reduction of gold chloride with formaldehyde. Further examination [39] of these sols has been carried out in relation to the factors influencing the size of the metal particles. As the concentration of reacting solution increases, the average size of the crystalline aggregates increases, although the unit crystals themselves decrease in size.

An important paper on reduction velocity and growth of the

[33] *Ber.*, 1925, **58**, 1539; *A.*, ii, 1090.

[34] *Loc. cit.*, 1542; *A.*, ii, 1072.

[35] *Kolloid-Z.*, 1925, **36** (*Zsigmondy Festschr.*), 230; *A.*, ii, 514.

[36] *Compt. rend.*, 1925, **181**, 419.

[37] *Kolloid-Z.*, 1925, **36** (*Zsigmondy Festschr.*), 103; *A.*, ii, 515; *ibid.*, p. 338; *A.*, ii, 782; *Rep. Imp. Ind. Res. Instit. Osaka, Japan*, 1925, **5**, 7; **6**, 9.

[38] *Kolloid-Z.*, 1925, **36** (*Zsigmondy Festschr.*), 341.

[39] *Ibid.*, p. 1; *A.*, ii, 196.

particles in the preparation of gold sols has been contributed by R. Zsigmondy and E. Hückel.[40] Mathematical theory is supported by experimental data on the formaldehyde reduction of gold salts either alone or containing definite quantities of a red gold sol. Rise of temperature, and, to a lesser extent, increase in formaldehyde or the nucleus sol, hastens reduction, this occurring in the immediate neighbourhood of the solid particles.

The mobility of the particles in gold hydrosols has been determined by P. A. Thiessen and J. Heumann,[41] who find a value of 3×10^{-4} cm./sec. under a potential gradient of 1 volt/cm., this value being independent of the method of preparation, particle size, and presence of protective colloids. When electrolytes such as barium chloride and strontium chloride are added, the mobility is reduced, but coagulation begins before complete discharge of the particles is effected.

L. Fuchs and Wo. Pauli[42] present a lengthy report of their work on the analysis and constitution of colloidal gold. The report deals with the Pauli theory of the chemical-complexity and origin of charge of colloid particles (*Die Zusammenfassung Naturwissenschaften*, 1924, **12**, 421, 548) as applied to various gold sols. The colloid particles are considered as being covered with a surface layer of "ionogenic gold complex," the dissociation of which gives rise to the negative charge.

A. Galecki,[43] in his "Physico-chemical Studies on Gold Sols," deals with sols prepared by several methods. Viscosity is named as the most important factor in colloid systems and the suggestion made that colloids divide on this basis into two great groups, the gold type and the protein type. Data are given relating to the viscosity and to the catalytic activity towards hydrogen peroxide of gold sols, correlating the results with the degree of dispersion of the metal. A Zsigmondy formaldehyde gold sol on ageing or flocculating shows a viscosity which passes through a minimum, but many experiments showed that exposure to light increases the viscosity of the sols. The catalytic decomposition of hydrogen peroxide is greater with fresh sols, especially as the alkali content is increased. Zsigmondy's "nuclear" sols have a catalytic effect directly proportional to the degree of dispersion.

Gold sols have been used by P. Uhlenbruck[44] to follow the decomposition of protein by pepsin. The change in colour of the

[40] *Z. physikal. Chem.*, 1925, **116**, 291; *A.*, ii, 775.
[41] *Z. anorg. Chem.*, 1925, **148**, 382; *A.*, ii, 1157.
[42] *Koll. Chem. Beihefte*, 1925, **21**, 195.
[43] *Kolloid-Z.*, 1925, **36** (*Zsigmondy Festschr.*), 154; *A.*, ii, 516.
[44] *Ibid.*, p. 287; *A.*, i, 742.

red gold sols runs parallel with the hydrolysis of protein, whilst the degree to which the flocculated gold is peptised is taken as a measure of the particle size of the decomposition products. H. A. Krebs [45] has shown that gold hydrosols may be precipitated by proteins in two ways: (*a*) the protein is more acid than at the isoelectric point, so that the positive colloid is mutually discharged with the negative gold; (*b*) a protein–gold complex may be formed. The protein concentration must be small in the first case, but has no limits in the second. The reactions are respectively irreversible and reversible (except in the isoelectric region), whilst the first gives a blue precipitate and the second a coarse, red precipitate.

Organosols.

E. Hatschek and P. C. L. Thorne [46] have extended their previous work on nickel sols in benzene and toluene (compare *A.*, 1923, ii, 645, 869), which showed that on heating nickel carbonyl in benzene or toluene containing rubber sols resulted containing both positive and negative particles. The pale green precipitate frequently observed in benzene or toluene solutions of nickel carbonyl is due to oxidation giving a hydrated basic nickel carbonate. In the presence of 0·17% of rubber such precipitation does not occur, but a green sol ensues, all its particles being positively charged. Further work is required to determine whether organosols in general contain oppositely charged ions, and also what is the origin of the charge. The presence of both positive and negative particles in a platinum–rubber sol has also been observed by F. Evers.[47] When the platinum is flocculated by cataphoresis, it is readily peptised again, frequently by simply standing for some hours in the liquid.

J. J. Bikerman [48] has prepared sols of arsenic trisulphide in nitrobenzene and in acetoacetic ester. Arsenic trichloride is dissolved in the organic liquid and dry hydrogen sulphide passed through. A stream of dry air then removes hydrogen chloride and excess hydrogen sulphide. Sols contained up to 29 millimols. of arsenic trisulphide per litre were quite stable, and had a conductivity of less than 10^{-7} mho. per cm. It was shown by cataphoresis tests that coagulation of the sol results when the electro-kinetic potential falls to 25×10^{-3} volt irrespective of the organic medium or the sol dilution. Ferric chloride, copper acetoacetic ester, and tetrapropylammonium iodide were used as coagulants. Bikerman states that the valence rule apparently holds for organosols if strongly ionised salts be used.

[45] *Biochem. Z.*, 1925, **159**, 311; *A.*, ii, 1155.
[46] *Kolloid-Z.*, 1925, **36**, 12; *A.*, ii, 197.
[47] *Ibid.*, p. 206.
[48] *Z. physikal. Chem.*, 1925, **115**, 261; *A.*, ii, 522.

According to F. S. Brown and C. R. Bury,[49] nitrobenzene sols of phosphoric oxide, calcium chloride, silica, alumina, and zinc chloride are formed in the presence of hydroxyl compounds such as alcohols or organic acids. The dehydrating agent adsorbs the OH– compound, thus becoming peptised. Organosols of grape sugar have been described by P. P. von Weimarn.[50] A 0·3% solution in acetone or 1% solution in ethyl alcohol is poured into excess of ether, benzene, toluene, or xylene, giving violet, deep blue, or green sols. Similarly a chromatic sol (the colour changing with variation in temperature) was obtained by heating glycerol with a solution of rubber in xylene.

A. Kuhn and H. Pirsch [51] prepared colloidal bismuth compounds in novel fashion. A mixture of the bismuth compound in lanolin was ground intensively at the temperature of liquid air, giving highly dispersed systems which could be diluted with sesame oil to form stable sols. In this way the sulphide, sulpho-iodide, and hydroxide sols were obtained containing 12—16 mg. of bismuth metal per 1 c.c.; 15—20% of lanolin is present as protective colloid. Electrical dispersions were also successful in organic media.

E. W. J. Mardles [52] in a paper on "The Swelling and Dispersion of Some Colloidal Substances in Ether–Alcohol Mixtures" treats of the important phenomenon that characteristic solvent action appears to be general with a large number of colloidal substances and *mixtures* of liquids. Any complete explanation must involve the significant fact that swelling precedes dispersion. The general principle is stated "that the characteristic solvent action of mixed liquids cannot be ascribed to the intrinsic action of one kind of molecule or molecular complex, but whenever molecular simplification occurs in a liquid mixture there is increased solvent action." Hence, loss of solvent power ensues when compound formation occurs between the components of a binary mixture. "The attraction between a colloidal particle and the molecules of the mixed dispersion medium, due to the presence of mutually reactive groups, appears to reach a maximum with certain combinations of liquids because of the special spatial arrangement and interlocking of the various molecules in the complex resulting from their size, from the relative strengths of their affinity bonds, etc., so that it is necessary to consider the relative specific characters of the liquid and the colloidal substance."

[49] *J. Physical Chem.*, 1925, **29**, 1312; *A.*, ii, 1055.
[50] *Kolloid-Z.*, 1925, **36**, 176.
[51] *Koll. Chem. Beihefte*, 1925, **21**, 78.
[52] *J.*, 1925, **127**, 2940.

Properties of Colloidal Systems.

Investigating arsenious sulphide hydrosol in relation to gravity settling, A. Dumanski [53] has observed over a period of four years a constant fall of the particles, calculated as a uniform rate of 0·031 cm. per day. The sol concentration was 0·0651 gram per c.c., and it stood in a glass tube 1 m. long by 2 cm. in diameter. The work of Porter and Hedges (*A.*, 1923, ii, 743) on the law of distribution of particles in colloidal suspensions was based on the assumption that no contraction or expansion occurs in the formation of a dilute suspension of gamboge in water. This assumption is justifiable according to the experiments made by J. R. H. Coutts,[54] who showed by actual density measurements that the simple additive law holds. W. W. Barkas [55] has shown that the formula used by Porter and Hedges holds within the limit of experimental error.

Mie's theory (*Ann. Physik*, 1908, **25**, 378) of the colour of metal sols has been mathematically developed by G. Jobst,[56] who deduces a radiation formula for a sol of completely reflecting spheres dispersed in a transparent medium. Gold sols were examined, the absorption and emission spectra being calculated for several sols with gold particles ranging in diameter from 100—600 μμ. Good agreement with values calculated from Mie's theory were obtained. The maxima in the curves flatten as the particles increase in size. The curves are correlated with the colours of the sols, the familiar red sol containing the large particles. The absorption curves for silver hydrosols have been studied by R. Feick, who finds Mie's original theory not in agreement with experiment. Qualitative agreement with the theory was found when the radiation and absorption of colloidal mercury were calculated from the data by Meyer (*Ann. Physik*, 1910, **31**, 1017).

In a valuable summary, H. Freundlich [57] deals with sols which contain non-spherical particles. A vanadium pentoxide sol shows double refraction in a magnetic field (Majorana phenomenon), and when stirred, streaks are seen due to dityndallism or double diffraction, the diffraction of light varying with the orientation of the rod-like particles in the liquid medium. The use of the azimuth diaphragm in the ultra-microscopic examination of such sols is indicated. Closely connected are the experiments of H. Zocher,[58] who observed that when hot concentrated solutions of benzo-

[53] *Kolloid-Z.*, 1925, **36**, 98; *A.*, ii, 290.
[54] *Trans. Faraday Soc.*, 1925, **21**, 63; *A.*, ii, 290.
[55] *Ibid.*, p. 66; *A.*, ii, 289. [56] *Ann. Physik*, 1925, **76**, 863; *A.*, ii, 777.
[57] Second Colloid Symposium, 1925, 46.
[58] *Z. anorg. Chem.*, 1925, **147**, 91; *A.*, ii, 966.

purpurin 4B and chrysophenin are cooled, the sols contained long, oriented particles. Brownian motion is maintained as a rapid oscillation about an equilibrium position. When placed in a magnetic field, the sols become anisotropic and reflect polarised light.

A. Frey [59] contributes a detailed discussion on the double refraction (birefringency) of colloids. It is shown that in a lyophilic system of the gelatin type, the disperse phase is present as isotropic, spherical micelles which can be deformed. Crystalline, anisotropic micelles characterise the lyophobe systems. These two classes of colloids differ as regards double refraction, although there is undoubtedly a gradual transition from the more or less emulsoid colloids like gelatin to the other extreme represented by vanadium pentoxide sols. The various cases of double refraction are summarised as: (i) double refraction due to form, due to oriented anisotropic particles small as compared with the wave-length of light. They may be parallel, circular cylinders or parallel, oblong rods. These give positive double refraction. Negative double refraction is due to connected lamellæ or to parallel plate micelles; (ii) residual double refraction which remains when the double refraction due to form is eliminated by using as continuous medium a liquid with the same refractive index as the particles; (iii) total double refraction, this being the sum of the two previously mentioned.

It has been shown by H. Freundlich and F. Oppenheimer [60] that on freezing hydrosols, the velocity of crystallisation of the water is usually increased by the presence of non-spherical disperse particles, but is increased by the presence of spherical particles. Twenty-two colloid systems (sols, emulsions, suspensions) were cooled to $-3°$ to $-7°$ and seeded with ice crystals. The results are explained on the theory of orientation of the water molecules at the surfaces of the disperse particles.

E. F. Burton and J. E. Currie [61] have studied the problem of the mutual action of charged particles in liquid media, and have recorded experimental evidence of mutual repulsion produced between similarly charged spheres in various liquids. Lead shot dropped through water, alcohol, benzene, toluene, and xylene carry a negative charge; through turpentine and carbon disulphide a positive charge, and through ether no charge. The experiments were applied to the detection of a scattering effect of the shot particles due to the possession of a charge.

[59] *Koll. chem. Beihefte*, 1925, **20**, 209; *A.*, ii, 200.
[60] *Ber.*, 1925, **58**, 143; *A.*, ii, 203.
[61] *Phil. Mag.*, 1925, **49**, 194.

Particle Size.

Hulet's well-known observation of the increased conductivity of a solution of barium sulphate has been repeated by D. Balareff,[62] who doubts that increase in solubility is to be attributed to the decrease in grain-size. He suggests that impurities liberated from the broken crystals, *e.g.*, barium chloride, may be the cause.

The size-frequency analysis of colloidal suspensions and powders continues to attract workers, and this subject is already establishing itself as an important branch of colloid technique. Its technical importance is obvious in relation to clays, soils, pigments, and the standardisation of manufacturers' products. An excellent survey of the methods available accompanies Sven Oden's mathematical analysis [63] of the grain-size frequency analysis. A bibliography of 41 papers is appended. Another useful summary is that of J. Parrish,[64] who devotes more attention to elutriation methods. A. Kuhn [65] describes ten methods (applicable to sols) including the measurement of light absorption, sedimentation weight, Brownian motion, osmotic pressure, ultrafiltration, dialysis, microscope and ultramicroscope enumeration, and *X*-ray analysis.

The Ostwald-von Hahn "flocculation meter" (*A.*, 1924, ii, 262) has been employed by R. Audubert and H. Rabaté,[66] W. J. Kelly,[67] and R. H. Lambert and E. P. Wightman.[68] The last authors describe a photographic recorder for following the sedimentation rate. Sedimentation analysis applied to photographic emulsions has been improved by F. F. Renwick and V. B. Sease. Sedimentation analysis has been employed in the grain-size analysis of clays [70] and tungsten powder.[71] The frequency curve based on the photographic study of blood corpuscles has been analysed by E. Ponder and W. G. Millar.[72] F. V. von Hahn [73] discusses the general problem of technical dispersoid-analysis, whilst an interesting paper by P. Drinker [74] gives details of measuring the particles of phagocytosed dusts and determining their size-frequency distribution.

[62] *Z. anorg. Chem.*, 1925, **145**, 122; *A.*, ii, 853. [63] *Soil Sci.*, 1925, **19**, 1.
[64] *J. Oil Col. Chem. Assoc.*, 1925, **8**, 195. [65] *Kolloid-Z.*, 1925, **37**, 365.
[66] *Compt. rend.*, 1925, **180**, 1663; *A.*, ii, 775.
[67] Second Colloid Symposium, 1925, 29.
[68] *J. Opt. Soc. Amer.*, 1925, **11**, 393.
[69] Second Colloid Symposium, 1925, 37.
[70] E. Schramm and E. W. Scripture, jun., *J. Amer. Ceram. Soc.*, 1925, **8**, 243.
[71] K. Agte, H. Schonborn, and K. Schroter, *Z. tech. Physik*, 1925, **6**, 293.
[72] *Quart. J. Expt. Physiol.*, 1925, **4**, 319.
[73] *Kolloid-Z.*, 1925, **37**, 377; see also F. Hebler, *ibid.*, 1925, **36**, 42.
[74] *J. Indust. Hygiene*, 1925, **7**, 305.

The globule-size analysis of emulsions has been investigated by A. J. Stamm,[75] using the Ostwald-von Hahn-Kelly sedimentation apparatus modified to deal with systems with a rising disperse phase. The same author collaborated with The Svedberg [76] to determine the globule-size frequency of emulsions using scattered light. The scattering of light (in the case of the emulsions studied—benzene in aqueous soaps) varies as the surface or square of the radius of the globules. An important paper by The Svedberg [77] concerns centrifuging, diffusion, and sedimentation analysis of colloids and substances of high molecular weight. The mathematics of grain-size analysis by means of the ultra-centrifuge is discussed as well as a new diffusion method.

Methods of Research.

Recent advances in dark-field illumination have been summarised by H. Siedentopf,[78] who describes the theoretical principles and some new dark-field condensers, including an oil-immersion lens with an internal iris diaphragm. Another paper on optical technique is due to H. Zocher,[79] who deals with the general question of anisotropy in disperse systems, its detection and measurement.

A useful instrument of research is the "kinoultramicroscope," a combination of the cinematograph and ultramicroscope. E. O. Kraemer [80] points out its advantages, such as obtaining a permanent objective record where, in the ordinary way, quantitative studies with the ultramicroscope alone frequently involve the use of statistical methods. He used the instrument for determining the size and the size-frequency of particles, investigating gel structure and recording the formation and coagulation of colloid particles.

X-Ray methods in colloid research have been dealt with by R. O. Herzog [81] and by H. Mark.[82] The former reviews recent work on the application of *X*-ray spectrography, particularly in connexion with the change liquid $\rightleftharpoons$ solid. Mark describes the experimental methods employed. *X*-Ray reflection of fatty acid films on glass furnished useful data relating to the molecular orientation of the fatty acids.[83]

The methods in use for determining the electric charge of colloid particles have been discussed by H. R. Kruyt [84] in a lucid and

[75] Second Colloid Symposium, 1925, 70; *A.*, ii, 1153.
[76] *J. Amer. Chem. Soc.*, 1925, **47**, 1582; *A.*, ii, 774.
[77] *Kolloid-Z.*, 1925, **36** (*Zsigmondy Festschr.*), 53; *A.*, ii, 528.
[78] *Ibid.*, 1925, **37**, 327. [79] *Ibid.*, p. 336.
[80] Second Colloid Symposium, 1925, 57; *A.*, ii, 1156.
[81] *Kolloid-Z.*, 1925, **37**, 355. [82] *Ibid.*, p. 351.
[83] J. J. Trillat, *Compt. rend.*, 1925, **180**, 280.
[84] *Kolloid-Z.*, 1925, **37**, 358.

well-illustrated paper. The methods include: (1) macroscopic cataphoresis of coloured sols, (2) macroscopic cataphoresis of non-coloured sols, *e.g.*, Svedberg's ultra-violet fluorescence method, (3) ultramicroscope examination of the cataphoretic velocity of single particles, (4) electric transport.

R. Auerbach [85] reviews the methods of diffusion analysis, whilst E. C. Bingham [86] deals with the subject of plasticity in colloid control.

Dialysis.

The permeability of various membranes for electrolytes has been investigated by L. Michaelis [87] and by A. Fujita,[88] both workers finding, by different methods, that the mobility of anions is much more reduced than that of kations. Michaelis enters into the theory of diffusion in considerable detail. W. Kopaczewski [89] gives the results of tests on the rate of diffusion of 53 dyes in 1% aqueous solution at 25° through a collodion membrane under standard conditions.

The use of tap-water in the dialysis of a hydrosol of silica with a parchment dialyser caused the sol to take up calcium, which, however, was easily removed by further dialysis against distilled water.[90] The results confirm the work of Gutbier, Huber, and Schieber (*Chem. Ztg.*, 1923, **47**, 110) that 80% of the electrolytes in a sol may be removed by a first dialysis with tap-water, which should be free from iron. The technique of dialysis has been described by H. Rheinboldt.[91] The principles underlying dialysis are dealt with and the special apparatus described are the electro-dialyser (Pauli), extraction dialyser (Golodetz), scaled dialyser (Gutbier and Mayer), vacuum dialyser (Golodetz).

Electro-dialysis claims considerable attention in modern work. E. Heymann [92] compares the rate of removal of strong electrolytes from sols and finds electrodialysis to be 10 times more rapid than ultrafiltration and 100 times more rapid than ordinary dialysis. L. Kofler and A. Wolkenberg [93] freed various saponins from electrolytes in this way. E. H. Harvey [94] reduced the ash-content of agar-agar from 3·75% to 0·81% (dry basis) by electrodialysis, whilst

[85] *Kolloid-Z.*, 1925, **37**, 379. [86] Second Colloid Symposium, 1925, 106.
[87] *J. Gen. Physiol.*, 1925, **8**, 33; *A.*, ii, 1150.
[88] *Biochem. Z.*, 1925, **159**, 370; *A.*, ii, 1151.
[89] *Rev. gén. Mat Col.*, 1925, **39**, 34, 105; *A.*, ii, 529.
[90] E. Wilke-Dorfurt and M. Decker, *Kolloid-Z.*, 1925, **36** (*Zsigmondy Festschr.*), 305.
[91] *Ibid.*, 1925, **37**, 387. [92] *Z. physikal. Chem.*, 1925, **118**, 65.
[93] *Biochem. Z.*, 1925, **160**, 398; *A.*, i, 1519.
[94] *Amer. J. Pharm.*, 1925, **97**, 66; *A.*, ii, 293.

W. F. Hoffman and R. A. Gortner [95] found that electrodialysis of agar-agar for 18 hours removes calcium, but leaves silica and sulphur unchanged.

Ultrafiltration.

A short bibliography and historical survey of the methods used in ultrafiltration have been given by H. Rheinboldt.[96] Summarising the methods and practical importance of ultrafiltration, L. Villa [97] recommend's Bechhold's impregnation of a porcelain filter with collodion or gelatin. Using gelatin, to retain colloidal platinum it is necessary for the membrane to have a concentration of 2%, for hæmoglobin 4%, and for deutero-albumose 10%. The mechanism of ultrafiltration is investigated by J. Duclaux and J. Errera,[98] who conclude that the membranes employed (nitrocellulose, denitrated nitrocellulose, and cellulose acetate) act as bundles of capillary tubes. Those liquids having no solvent or softening action on the membranes filter at a rate proportional to their viscosities. L. Zacharias [99] also discusses the mechanism of ultrafiltration, dealing especially with (1) the support for the membrane, (2) the membrane itself. Using collodion under standard conditions, he found the permeability of the membrane directly proportional to the porosity of the support. Filtration rate is proportional to the number of layers of collodion deposited. A liquid which causes the membrane to swell induces opposing effects, the pores open but they also lengthen, so that in some instances compensation occurs and no extra permeability ensues. Unglazed porcelain carrying barium sulphate in its pores acts as an ultrafilter without the need of a membrane. Swelling or stretching is avoided in such a filter.

E. Fouard [1] has devised a collodion ultrafilter capable of standing 40 atm. pressure, the membrane pores having diameters of the order 1 μμ. Another apparatus designed to yield a uniform membrane with gelatin or collodion is described by E. Müller.[2] Stirring speeds up the ultrafiltration of solutions when high pressures are required, and for this purpose two forms of electromagnetic stirrers have been described by B. Bruckner and W. Overbeck.[3]

A combination of ultrafiltration and electro-dialysis has been used by H. Bechhold and A. Rosenberg [4] to purify gelatin and

[95] *J. Biol. Chem.*, 1925, **65**, 371; *A.*, ii, 1158.
[96] *Kolloid-Z.*, 1925, **37**, 392.
[97] *Arch. di. Patalog e. Clin. Medica*, Sept., 1925, p. 425.
[98] *Rev. gén. Coll.*, 1925, **3**, 97; *A.*, ii, 530.
[99] *Kolloid-Z.*, 1925, **37**, 50.
[1] *Ann. Chim. Anal.*, 1925, **7**, 33.
[2] *Kolloid-Z.*, 1925, **37**, 237; *A.*, ii, 1061.
[3] *Ibid.*, 1925, **36** (*Zsigmondy Festschr.*), 192.
[4] *Biochem. Z.*, 1925, **157**, 85; *A.*, ii, 668.

glue. A modification is the use of the electro-dialyser with an ultrafilter at both the anode and kathode, permitting rapid removal of salts. The method has advantages over the usual ultrafiltration technique.[5] The probability that the protoplasmic permeability of lipoid-insoluble substances is due to an ultra-filtration process is discussed by R. Collander,[6] who has also investigated the permeability of the copper ferrocyanide membrane to acids.

An important paper on the ultrafiltration of non-aqueous systems has been contributed by H. Bechhold and V. Szidon.[7] By the Bechhold-Konig method (*Z. angew. Chem.*, 1924, 494) ultrafilters for non-aqueous solutions were prepared (amongst others) by impregnating porous-clay filters with ether solutions of collodion which were then coagulated by benzene or toluene. Oil sols of zinc and cadmium sulphides, ferric oxide, graphite, and iron and copper oleate were thus ultrafiltered, as well as a number of dyes soluble in organic liquids. It was shown that the dye solutions contain only a small portion as colloidally dispersed dye. The porosity of the ultrafilters was determined by two methods, these giving concordant results. The first method is to ultrafilter various colloid solutions of known particle size, and the second or "air-bubble method" is based on the maximum pressure required to force air through the ultrafilter.

Viscosity.

The work of several investigators on the measurement of the viscosity of colloid systems has been summarised by N. R. Dhar,[8] whilst the technique of the subject is reviewed by W. Stauf.[9] Wo. Ostwald [10] has investigated the velocity function of the viscosity of disperse systems. The deviations of the viscosity of colloid systems from the Hagen-Poiseuille law are due to factors included in the general term "structural viscosity," evidence for which is given by the variations of pressure or velocity of flow when a capillary viscosimeter is used for measuring viscosity. The velocity function of the viscosity of different colloidal solutions may be quantitatively expressed by an extension of the Hagen-Poiseuille law of the general form :

$$V^{1/n} = kp \quad \text{or} \quad \eta = kp^n \,.\, t.$$

Here V = the velocity of deformation or of flow (quantity/time),

[5] H. Bechhold, *Z. Elektrochem.*, 1925, **31**, 496; *A.*, ii, 1158.
[6] *Koll. Chem. Beihefte*, 1925, **20**, 273; *A.*, ii, 201.
[7] *Kolloid-Z.*, 1925, **36** (*Zsigmondy Festschr.*), 259; *A.*, ii, 529.
[8] *J. Physical Chem.*, 1925, **29**, 1556.
[9] *Kolloid-Z.*, 1925, **37**, 397.
[10] *Ibid.*, 1925, **36**, 99; 157; 248; *A.*, ii, 291, 392, 663.

p = the pressure, t = time, η = the total experimentally-determined resistance to deformation (or the viscosity), and k and n are constants. The Ostwald capillary viscosimeter is recommended, but the equation agrees with measurements made with the Hess apparatus to within 1—2%. The Couette apparatus also gives results which fit the equation. Considerable experimental data is recorded and the work of many other workers referred to. R. Auerbach [11] describes a capillary viscosimeter for use with a variable velocity of flow. The viscosity of water obeyed the Hagen-Poiseuille law, but 1% gelatin solution did not. The results with gelatin correspond with the Ostwald exponential equation, provided the pressures are less than about 0·5 m. The change in viscosity with the rate of shear has been studied by A. de Waele,[12] who measured the viscosity of oil sols of mineral earths with a rotation viscosimeter. The viscosity increased as the rate of rotation was increased.

In an interesting account of the determination of viscosity of lyophile colloids, H. R. Kruyt [13] describes a modification of the Ostwald viscometer. He found that agar and gelatin sols obey Poiseuille's law only when at a temperature above their gelatinising point. Hydrosols of starch, gum arabic, casein, ceria and silica obey the law, but vanadium pentoxide sols on ageing show marked deviations. It is concluded that sols containing spherical primary particles obey Poiseuille's law, deviations occurring when the spherical form is departed from.

E. Hatschek,[14] dealing with the variable viscosity of a two-phase system, shows that viscosity may decrease as the rate of rotation increases owing to the formation of solvent films around the dispersed particles, these films partly breaking down on rapid rotation.

Peptisation and Protection.

A. V. Slater [15] has classified numerous references to peptisation in an endeavour to return strictly to Graham's use of the term. The author's definition is, "true peptisation is the transformation of a gel to a sol by addition of a small quantity of a dispersing agent." In addition to increased electric charge and lowered interfacial tension, a "true solution pressure" comes into play, the colloid particles being drawn into solution by the solution pressure exerted by the peptiser. A theory of peptisation is also put forward by

[11] *Kolloid-Z.* (*Zsigmondy Festschr.*), p. 252; see also K. Matthäus, *ibid.*, p. 281; *A.*, ii, 663.

[12] *Ibid.*, p. 332; *A.*, ii, 777.

[13] *Ibid.* (*Zsigmondy Festschr.*), p. 218; *A.*, ii, 515.

[14] *Ibid.*, 1925, **37**, 25.

[15] *J. Soc. Chem. Ind.*, 1925, **44**, 499T.

K. C. Sen,[16] the theory assuming a high degree of adsorption and a suitable concentration of electrolyte. Omitting non-aqueous systems in which the stability conditions are still obscure, Sen believes that practically all the known cases of colloid formation in solution can be explained as cases of ion peptisation or peptisation by means of an ion-peptised colloid. It is extremely doubtful whether non-electrolytes can peptise a substance, and peptisation by an undissociated salt is improbable. The theory is extended in a further paper [17] and the nature of the protective action raised. Sen believes that protective colloids confer stability owing to a Helmholtz double layer between the colloid particle and the medium.

J. Traube and E. Rackwitz [18] have carried out important experiments on protective colloids. Protective action is considered to relate to three adhesion forces, *viz.*, between the protective colloid and water, between the initial unprotected colloid and water, and between the two colloids. Capillary-active substances possess a decidedly smaller adhesion-force towards water than do the capillary-inactive substances, whence one would expect the protective action for hydrophobe sols to be greater with gelatin, albumin, dextrin (capillary-inactive) than with saponin, soap, bile-salts (capillary active). Proof of this theory was established by determining the "hydrosol number" after the manner of Zsigmondy's gold number, *i.e.*, determining the amount of protective colloid required to protect sols of gold, silver, carbon, ferric hydroxide, Prussian blue, sulphur and arsenic trisulphide. It was found that the capillary-active colloids had an essentially smaller protective effect than the capillary-inactive for hydrophobe sols such as gold, silver, or carbon, but, as anticipated, this difference does not occur for sols of sulphur and arsenic trisulphide, *i.e.*, colloids with a smaller adhesion-force for water. Further interesting experimental work supports the theory.

The chemical adsorption theory of protective action finds support in experiments by S. S. Bhatnagar, M. Prasad and D. C. Bahl,[19] who measured the surface tension of soap solutions of various concentrations with and without such colloids present as arsenic, antimony, and cadmium sulphides. Marked adsorption of soap was evidenced. Similarly, it has been observed that sugars are adsorbed by the particles in hydrosols of these sulphide sols and selenium metal hydrosol.[20]

[16] *J. Physical Chem.*, 1925, **29**, 1533.
[17] *Kolloid-Z.*, 1925, **36**, 193; *A.*, ii, 666.
[18] *Ibid.*, 1925, **37**, 131; *A.*, ii, 968.
[19] *J. Ind. Chem. Soc.*, 1925, **2**, 11; *A.*, ii, 1155.
[20] *J. Physical Chem.*, 1925, **29**, 166; *A.*, ii, 293.

The protective effect of gelatin on gold hydrosols varies with the p_H of the solution. H. V. Tartar and J. R. Lorah [21] find protection most marked when the gelatin is at the isoelectric point or possesses a negative charge. Below p_H 4·7, the gelatin becomes positively charged and its protective power falls rapidly as the p_H decreases. Between p_H 5 and 8 the hydrogen-ion concentration has practically no influence on the protective action.

B. Papaconstantinou [22] has investigated the protective action of soaps on gold hydrosols. For 0·1% sodium oleate at 14° protective action decreased as the size of the gold particle increased. A series of soaps was examined, the gold number being determined at different temperatures. For sodium and potassium laurate, myristate, palmitate, stearate, and oleate, the gold number is reduced as temperature rises, *i.e.*, protective action is enhanced. Sodium and potassium linoleates show the reverse effect. Similar results have been obtained with arsenious sulphide sol in place of the gold sol.[23]

W. Reinders,[24] by determining the gold number of proteins at varying p_H values, correlates the protective effects with the amphoteric nature of the proteins. An interesting observation is recorded by A. Boutaric and G. Perreau,[25] who protected gamboge suspension by addition of electrolytes in amounts too small to effect flocculation. If to this protected suspension, electrolyte is further added until flocculation results, the amount of electrolyte required for this effect is greater than is normally the case with an untreated suspension. In a later paper,[26] a table is given relating to the protective action of the chlorides of uni-, bi-, and ter-valent metals, sodium silicate and alkalis on arsenic trisulphide sol against flocculation by sulphuric acid and chlorides.

Coagulation.

It is suggested by A. de G. Rocasolano [27] that the ultramicroscope observations of Brownian motion provide a ready means of studying flocculation changes. A qualitative and quantitative study of the effect of stirring on the coagulation of hydrophobic sols has been made by H. Freundlich and S. K. Basu.[28] Copper oxide sol was

[21] *J. Physical. Chem.*, 1925, **29**, 792; *A.*, ii, 864.

[22] *Kolloid-Z.*, 1925, **36** (*Zsigmondy Festschr.*), 329; *A.*, ii, 526; *J. Physica Chem.*, 1925, **29**, 319; *A.*, ii, 393.

[23] *J. Physical Chem.*, 1925, **29**, 323; *A.*, ii, 393.

[24] *Chem. Weekblad*, 1925, **22**, 481; *A.*, ii, 1059.

[25] *Compt. rend.*, 1925, **180**, 1337. Also in *Rev. gén. Coll.*, 1925, **3**, 129, 167; *A.*, ii, 526, 778, 863.

[26] *Compt. rend.*, 1925, **180**, 1841.

[27] *Kolloid-Z.*, 1925, **36** (*Zsigmondy Fcstschr.*), 80; *A.*, ii, 523.

[28] *Z. physikal. Chem.*, 1925, **115**, 203; *A.*, ii, 522.

used in the quantitative work, the other experiments being done with sols of arsenic trisulphide, ferric oxide, vanadium pentoxide, and gold. The larger the particles of the sol, the more does stirring favour coagulation. Its influence is pronounced also when the electrolyte is in high concentration and when ions of the marked flocculating power are used. These and other experiments of much interest support Smoluchowski's theory of coagulation velocity.

The views of L. Michaelis on the "General Principles of Ion Effects in Colloids" are lucidly summarised in a lengthy paper.[29] Two effects are recognised: the electrostatic effect, depending on the valency of the ions and almost entirely due to the ions bearing a charge opposite to that of the colloid. The lyotropic effect, which is more pronounced with hydrophilic colloids, depends on the water attracting power of the ions. It does not depend on the charge sign and only becomes evident in relatively high concentrations of electrolytes. In contrast to this, the electrostatic effect may occur in very dilute solutions.

According to W. O. Kermack and W. T. H. Williamson,[30] the rate of sedimentation of kaolin suspensions under the influence of various salts is markedly affected by variations in hydrogen-ion concentration. As a rule, the decrease in the p_H value favours sedimentation. With sodium chloride, however, sedimentation is increased by a rise in p_H, whereas potassium chloride hastens sedimentation at all p_H values. Chemical actions probably complicate the phenomena.

In the coagulation of negative and positive colloids by acids and bases, Perrin's rule (*J. Chim. Phys.*, 1905, **3**, 50) is that the solutions possessing equal flocculating power contain the same number of hydrogen or hydroxyl ions, as the case may be. Notable exceptions to this rule are recorded by G. Rossi and M. Andreanelli,[31] who believe the phenomenon cannot be purely electrical.

A. B. Weir[32] has investigated the critical concentrations of hydrochloric, sulphuric, acetic, and citric acids necessary completely to coagulate a sol of Prussian blue. Citric acid is normal in its behaviour, contrary to the results of Bradfield (*J. Amer. Chem. Soc.*, 1923, **45**, 1243). There was no apparent stabilising effect of the different anions, a conclusion also reached by Tartar and Gailey (*ibid.*, 1922, **44**, 2212), who worked with gamboge and mastic suspensions. With oxalic acid, however, a strong protective adsorption of the anion is indicated.

Considering the mechanism of the adsorption of ions by colloidal

[29] Second Colloid Symposium, 1925, 1.
[30] *Proc. Roy. Soc. Edin.*, 1925, **45**, 59; *A.*, ii, 523.
[31] *Gazzetta*, 1925, **55**, 99; *A.*, ii, 394.
[32] *J.*, 1925, **127**, 2245.

particles, R. Audubert and M. Quintin [33] give evidence for the view that the adsorption equilibrium is fundamentally dependent on electrostatic and osmotic forces and has nothing to do with the nature of the surface or with chemical action between the adsorbent and the adsorbed reagent.

W. O. Kermack and C. I. B. Voge [34] have studied the action of salts with multivalent kations on hydrosols of gold and gum benzoin. It was observed that "salts of tervalent kations are able to confer, under appropriate conditions of concentration and p_H, a positive change on the particles of a negatively charged sol." A zone of precipitation separates the regions wherein the sol particles are negatively and positively charged, respectively. These zones are closely connected with the degree of hydrolysis of the salts.

K. C. Sen,[35] discussing the antagonistic action of electrolytes on colloidal solutions, states the general rule that if an ion bearing the same charge sign as the colloidal particles is more strongly adsorbed or at certain concentrations becomes concentrated at the interface between the two phases, then the charge and dispersion of the suspension will be increased. The action of oppositely charged ions in the system will thus be opposed. If, however, the oppositely charged ion is adsorbed in excess, coagulation occurs with a suspension and phase-reversal with an emulsion.

Smoluchowski's equation of coagulation velocity is confirmed by C. K. Jablczyński and P. Przezdziecka-Jedrzejovska [36] by experiments on the coagulation of antimony trisulphide hydrosol with potassium chloride. Interesting comparison of the conditions of electrolyte coagulation of hydrosols of arsenic trisulphide, selenium, and tellurium with Oden's sulphur hydrosols have been made by J. J. Doolan.[37] Discussing the many factors influencing sol flocculation, the author believes that no general law holds for the quantitative effects of ions.

The coagulation of arsenic trisulphide sol by barium chloride points to the conclusion, according to A. J. Rabinovitsch,[38] that the sol is a fairly strong complex acid dissociating into $(As_2S_3)_nSH'$ and $H^{\cdot}$. The coagulation of negatively charged stannic hydroxide hydrosol by means of electrolytes follows the Schulze-Hardy rule, with the exception of thorium nitrate. As the sol concentration decreases, the precipitation value of the electrolytes also diminishes.

[33] *Compt. rend.*, 1925, **180**, 513.
[34] *Proc. Roy. Soc. Edin.*, 1924—1925, **45**, 90; *A.*, ii, 523.
[35] *Z. anorg. Chem.*, 1925, **149**, 139.
[36] *Bull. Soc. chim.*, 1925, **37**, 608; *A.*, ii, 665.
[37] *J. Physical Chem.*, 1925, **29**, 178; *A.*, ii, 293
[38] *Z. physikal. Chem.*, 1925, **116**, 97; *A.*, ii, 778.

Several exceptions to this rule were found and correlated with the adsorption by the sol particles of ions of the same sign. Similar results were obtained using hydrosols of Prussian blue and ferric oxide.[39]

The influence of adsorbed anions on the coagulation of hydrosols of arsenic and antimony trisulphides is discussed by S. Ghosh and N. R. Dhar,[40] whilst K. C. Sen and M. R. Mehrotra [41] deal with the influence of stabilising ions in the coagulation of hydrosols of chromium hydroxide and copper ferrocyanide. Similar work on ion antagonism when mixed electrolytes are used to coagulate arsenic trisulphide sol has been carried out by J. N. Mukherjee and B. N. Ghosh.[42] S. Ghosh and N. R. Dhar [43] believe that the abnormal behaviour of diluted sols towards coagulation by mixed electrolytes must be attributed to the adsorption of stabilising ions of the same sign of charge as the sol.

The rate of coagulation of mixed colloids has been investigated by K. Jabłczyński and H. Lorentz-Zienkovska.[44] It was found that the velocity of coagulation proceeds according to the same law as for each sol separately, the experiments being conducted with arsenic and antimony trisulphide hydrosols. It is believed that coagulation is a purely physical phenomenon.

An interesting case of coagulation has been reported by H. Freundlich and F. Moor.[45] Arsenic trisulphide hydrosol and Carey Lea's silver hydrosol when mixed give a colloidal solution which undergoes colour change and shows alterations when studied under the ultramicroscope. The reactions which occur in the light and in the dark are different. The dark reaction most probably depends on the union of the silver and arsenic trisulphide particles. All the particles are negatively charged, but, in spite of this, they come together owing to a strong chemical affinity. The reaction in light is purely chemical and oxygen is a co-operating factor. It is suggested that a silver thioarsenite is formed.

Sensitisation.

The phenomenon of the sensitisation of a colloidal solution towards coagulation continues to draw attention. An excellent summary appeared by H. Freundlich in "Colloidal Behaviour" (Bogue), Vol. I, pp. 297—323.

[39] S. Ghosh and N. R. Dhar, *J. Physical Chem.*, 1925, **29**, 435, 659; *A.*, ii, 78.

[40] *Kolloid-Z.*, 1925, **36**, 129; *A.*, ii, 386.

[41] *Z. anorg. Chem.*, 1925, **142**, 345; *A.*, ii, 665.

[42] *J. Indian Soc. Chem.*, 1925, I, 213; *A.*, ii, 394.

[43] *J. Physical Chem.*, 1925, **29**, 435; *A.*, ii, 511.

[44] *Bull Soc. chim.*, 1925, **37**, 612; *Rocz. Chem.*, 1925, **5**, 178; *A.*, ii, 666, 1060.

[45] *Kolloid-Z.*, 1925, **36**, 17; *A.*, ii, 198.

W. Beck [46] finds that lecithin or cholesterol added to ferric oxide hydrosol (positive) or molybdenum pentoxide hydrosol (negative) sensitises electrolyte coagulation. Lecithin sensitised Congo-red hydrosol but cholesterol protects this particular sol. G. Ettisch and H. Runge [47] dispute Beck's claim that lecithin sensitises Congo-red hydrosol and they also give data showing that globulin is also without effect, although Brossa (*Kolloid-Z.*, 1923, **32**, 107) reported sensitisation. The discrepancies in the results of various workers in this connexion are due to the salt content and the p_H value of the systems used.

The fact that gelatin may sensitise or protect a hydrosol of cholesterol depends on the concentration of the gelatin. According to W. O. Kermack and P. MacCallum,[48] the protective gelatin layer is unimolecular. When, however, "precipitation takes place, the amount of gelatin present is insufficient to form even a unimolecular layer, although there is sufficient partially to neutralise the electric charge on the cholesterol particle." The particles cease to repel one another "and having part at least of their surfaces bare and cohesive, are precipitated." The experimental work included the determination of the cataphoretic *P.D.* between the cholesterol particles and the medium in the presence of gelatin at various concentrations and at various p_H values.

Using a negatively charged copper ferrocyanide hydrosol, K. C. Sen [49] observed that sucrose sensitised its coagulation with barium chloride, but not with potassium chloride. Ethyl and propyl alcohols sensitised the sol towards all coagulating ions.

A mastic hydrosol is sensitised by sodium chloride towards coagulation by *X*-rays, the longer waves having a more pronounced action than the shorter waves.[50]

Gelatin.

The peculiar position occupied by gelatin in colloid chemistry is reflected in the very active research in many directions. The influence of neutral salts on the combination of gelatin with hydrochloric, nitric, and sulphuric acids has been studied by J. Csapó,[51] who finds that $K^{\cdot} > Na^{\cdot} > Ba^{\cdot\cdot} > Ca^{\cdot\cdot}$ increases the combination, as do also Cl', NO_3', and I', but not SO_4'', this decreasing it. Neutral salts also influence the swelling of isoelectric gelatin, the Hofmeister

[46] *Biochem. Z.*, 1925, **156**, 471; *A.*, ii, 527.
[47] *Kolloid-Z.*, 1925, **37**, 26; *A.*, ii, 864.
[48] *Proc. Roy. Soc. Edin.*, 1924–25, **45**, 71; *A.*, ii, 525.
[49] *J. Physical Chem.*, 1925, **29**, 516; *A.*, ii, 664.
[50] A. Dognon, *Compt. rend. Soc. Biol.*, 1924, **21**, 197; *A.*, ii, 665.
[51] *Biochem. Z.*, 1925, **159**, 53; *A.*, ii, 1157.

series holding.[52] Though the p_H has effect on the swelling, the neutral salt action masks this, and Loeb's view that swelling is due to p_H alone is erroneous. The increased dispersion of gelatin by neutral salts is shown by data gathered from ultrafiltration, specific rotation, viscosity, dialysis, gold number, and tannin precipitation test.[53] The proteolytic activity of trypsin on gelatin at 37° is unaffected by the presence of neutral salts, except that N- and $2N$-sodium thiocyanate cause a slight decrease.[54]

Two papers deal with the surface tension of gelatin solutions. J. H. S. Johnston and G. T. Peard [55] find that rise in temperature and presence of electrolytes decrease surface tension. Surface tension data show two maxima, at p_H 4·7 and p_H 2·8 to 3·0, minima being observed at p_H 3·8 to 4·0 and p_H 9·0. These results are independently confirmed by L. de Caro,[56] who agrees with Bottazzi and d'Agostino (*A.*, 1913, ii, 115) that the non-dissociated form of the gelatin effects the most marked lowering of surface tension.

Instead of the isoelectric point of gelatin being at p_H 4·7, I. I. Shukov and S. A. Stschoukarev [57] find the value p_H 5·6, and they assume that gelatin is a mixture of two substances with different isoelectric points. Several instances occur in the literature showing that at p_H 7·8, gelatin exhibits discontinuity in swelling, light absorption, gel strength, and titration curve. E. O. Kraemer [58] examines this problem and believes there is some important change in the system at this p_H. His conclusion is that "the second 'isoelectric point' of gelatin at a p_H 7·8 should be due to a neutralisation of the electro-kinetic potential difference with a reversal in sign at p_H 7·8. The discontinuity in swelling and other physical properties at this point would therefore reflect the influence of the electrokinetic potential upon these properties." No second isoelectric point at this p_H could be found by R. H. Bogue and M. T. O'Connell.[59] Determinations of the specific rotation of 2% solutions of originally isoelectric and ash-free gelatin at 30° at p_H values ranging from 0·3 to 13·4 showed the specific rotation to vary with p_H. The rotation is low at high concentrations of acid or alkali, rising as the acidity or alkalinity decreases, and exhibiting a minimum value at the isoelectric point, p_H 4·7. A detailed study of the optical activity of gelatin systems has been made by E. O. Kraemer and J. R. Fanselow,[60] who conclude that there is not sufficient evidence

[52] E. Stiasny and S. R. D. Gupta, *Collegium*, 1925, 13; *A.*, ii, 392.
[53] *Idem, ibid.*, 23; *A.*, ii, 393. [54] *Idem, ibid.*, 57.
[55] *Biochem. J.*, 1925, **19**, 281; *A.*, ii, 659.
[56] *Atti R. Acad. Lincei*, 1925, **1**, 729; *A.*, ii, 857.
[57] *J. Physical Chem.*, 1925, **29**, 285; *A.*, ii, 386.
[58] *Ibid.*, p. 410; *A.*, ii, 519.
[59] *J. Amer. Chem. Soc.*, 1925, **47**, 1694; *A.*, ii, 744.
[60] *J. Physical Chem.*, 1925, **29**, 1169; *A.*, ii, 1057.

for the statement of other workers that gelatin contains two related molecular species. F. Vlès and E. Vellinger,[61] investigating the rotary power of gelatin at different p_H values (prepared by Loeb's method), found the diffusion of light to be a maximum at p_H 4·7; two minima occur at p_H 2·6 and p_H 13. In the case of collagen, A. W. Thomas and M. W. Kelly[62] give evidence that two modifications exist, "gel" and "sol," the latter developing in solutions at 40°, with an isoelectric point at about p_H 8.

Loeb's work on the significance of the hydrogen-ion concentration in the swelling of gelatin has been criticised by Wo. Ostwald, A. Kuhn, and E. Böhme.[63] Three different gelatins, including pure isoelectric gelatin, were examined in relation to swelling as influenced by different acids. Concentration and p_H value being maintained constant, swelling differed in different acids. The swelling of isoelectric gelatin was influenced in the gradation hydriodic acid>glycerophosphoric acid>sulphosalicylic acid>hydrochloric acid>sulphuric acid. Contrary to Loeb's view, dibasic acids can exert a greater influence than monobasic acids, in a certain p_H range, and the difference between the swelling effects of monobasic and dibasic acids is always less than that between different monobasic acids. In mixtures of salts and acid there is a marked anion effect on the gelatin swelling, the Hofmeister ion series being followed. The swelling of gelatin in aqueous solution is increased by the presence of formalin, glycerol, phthalic acid, and by magnesium and manganese salts, there being an optimum concentration in each case.[64]

Several workers have investigated the elasticity of gelatin gels. H. J. Poole[65] contributes an important paper characterised by the experimental technique employed in dealing with jellies. The author concludes: "The strain produced in gelatin jellies by the application of a steady stress is not a function of that stress alone as in the case of perfectly elastic bodies, but is governed by a time factor. The results of a study of this time factor or 'creep' give support to the theory that the jellies are two-phase (solid-liquid) bodies. It is shown that the creep is mainly due to a reversible flow of the liquid phase in the interstices of the solid phase and, to a lesser extent, to an irreversible plastic deformation of the solid phase." The solid phase is considered to be in the form of a mesh of cylindrical fibrils or threads, the material of the threads being in dynamic equilibrium with the water of the liquid phase. The

[61] *Compt. rend.*, 1925, **180**, 439; *A.*, ii, 292.
[62] *J. Amer. Chem. Soc.*, 1925, **47**, 833; *A.*, ii, 520.
[63] *Koll. Chem. Beihefte*, 1925, **20**, 412; *A.*, ii, 777.
[64] M. Popov and K. Seisov, *Biochem. Z.*, 1925, **156**, 97; *A.*, i, 606.
[65] *Trans. Faraday Soc.*, 1925, **21**, 114; *A.*, ii, 519.

ratio of gelatin in the solid phase to that in the liquid phase will be progressively less as the temperature is raised.

G. W. Scarth [66] determined the relation of the elasticity of gelatin to p_H by the method of transferring pre-formed gels from a medium of one p_H to one of another p_H, and comparing the extensibility under a given stress after volume change is more or less completed. The reciprocal of the extension has a minimum value at p_H 4·7, and maxima at about p_H 3 and 11, the latter maximum being the higher. Young's modulus in the case of isotropic gelatin varies very little between p_H 4·7 and p_H 11, falling slightly on the acid side of the isoelectric point. Three separate factors affecting elasticity are involved in p_H change : (1) direct action of the reagent in combining chemically or by adsorption with the gelatin, (2) the modification of imbibition resulting from such combination, (3) structural changes induced by these effects. Scarth infers that gelatin gels possess a heterogeneous structure which is modified by swelling agents as well as by heat. The major variations in the degree of swelling must be due to changes in a positive force attracting water.

Details of a method for determining the elasticity of gelatin gels have been given by E. Sauer and E. Kinkel,[67] who find that with pure gelatin the modulus of elasticity varies at the square of the concentration, but for lower-grade gelatins as the nth power of the concentration, n being characteristic for a given gelatin.

A series of papers by S. Yumikura deals with the rate of diffusion of capillary active and inactive substances into gelatin gels.[68]

Previous work by R. Wintgen and H. Löwenthal (*Kolloid-Z.*, 1924, **34**, 289) having shown that gelatin and colloidal chromic oxide mutually precipitate each other to an extent depending on the degree of dispersity and the concentration, the subject has now been extended to the use of iron hydroxide sols, and the conditions of precipitation have been worked out.[69] The precipitation of gelatin by tannin again receives attention. I. A. Smorodincev and A. N. Adova [70] find that p_H has a distinct influence. The more acid the gelatin sol the better is the precipitation. At p_H 10·06, a 0·035% gelatin sol gives no precipitate with tannin. No precipitate forms at p_H 7 if the gelatin is less concentrated than 0·003%, whilst at p_H 8·95, a concentration below 0·013% fails to give a precipitate.

[66] *J. Physical Chem.*, 1925, **29**, 1009; *A.*, ii, 862.
[67] *Z. angew Chem.*, 1925, **38**, 413; *A.*, ii, 519.
[68] *Biochem. Z.*, 1925, **157**, 359, 371, 377, 383; *A.*, i, 735.
[69] R. Wintgen and E. Meyer, *Kolloid-Z.*, 1925, **36** (*Zsigmondy Festschr.*), 369; *A.*, ii, 524.
[70] *Z. physiol. Chem.*, 1925, **144**, 255; *A.*, i, 847.

H. B. Stocks and C. V. Greenwood [71] have observed that the carbohydrate—tragasol—is precipitated by tannin in similar manner to gelatin. It was shown that gelatin films will imbibe solutions of tannin, but do not combine with the tannin.

Jellies.

P. P. von Weimarn's views relating to "the jelly condition of matter" have been confirmed by experiments on disperse systems of soaps in dry toluene. He regards the formation of a jelly as an extreme case of crystallisation.[72]

It is a peculiarity of concentrated ferric oxide hydrosols that with suitable amounts of electrolytes they set to pasty gels which liquefy on shaking and re-set again on standing, the time taken in the second setting being measurable and reproducible. It depends on the anion valency. The kinetics of this sol–gel change forms the subject of an important paper by H. Freundlich and A. Rosenthal,[73] the question being: Can one reach a region of constant setting velocity when increasing electrolyte additions are made to concentrated ferric oxide hydrosols? It was found that increasing the concentration of electrolyte (potassium chloride) did not alter the value of the setting velocity.

E. O. Kraemer [74] has critically studied the question of the structure of gelatin gels and concludes that "gel formation is the result of an incomplete or unsuccessful attempt at precipitation of a solid phase from a liquid system." Regarding the micro-structure of the gels and the order of magnitude of the discontinuities within them, optical properties and general behaviour indicate a rather fine-grained structure, but other considerations show that "on a molecular scale such gels do not possess the high rigidity which they display in bulk." Cinematograph records were made of the Brownian movement of mercury particles (200—250 $\mu\mu$ radius) in the gels, from which the author concludes that the structure of weak gelatin gels is still considerably finer than the indicating mercury particles and their displacements. R. H. Bogue [75] approves the theory of a fibrillar structure for gelatin gels.

Swelling phenomena have been further investigated, methods for the quantitative estimation of swelling being outlined by P. A. Thiessen.[76] The kinetics of swelling and shrinkage of gels have

[71] *J. Soc. Leather Trades Chem.*, 1925, **2**, 315; *A.*, i, 1165.
[72] *Kolloid-Z.*, 1925, **36**, 175; *A.*, ii, 390.
[73] *Ibid.*, 1925, **37**, 129; *A.*, ii, 967.
[74] *J. Physical Chem.*, 1925, **29**, 1523.
[75] *Ibid.*, 1925, **29**, 1233; *A.*, ii, 1058.
[76] *Kolloid-Z.*, 1925, **37**, 406.

been studied by I. S. Liepatov [77] and by W. Biltz,[78] the latter using equations based on the conception of lattice energy.

E. Hatschek [79] prepared square prisms of gelatin gels, and, after setting, these were twisted or bent and so permanently deformed. Subsequent drying increased the deformation. If, however, the initial gel were set in a twisted form, no further deformation resulted on drying, thus showing that in the former experiments the increased deformation was due to the applied stress on the set gel, and not to its shape. Similar work on the course and character of shrinking has been reported by K. Schaum,[80] who, however, worked with gelatin drops, dried on surfaces such as mercury and glass.

B. L. Clarke [81] has presented the general form of the curve relating swelling capacity of agar-agar gels to the water content immediately before swelling. The curve shows a well-defined maximum. Other papers on gels deal with: (*a*) double refraction and dichroism of stained gels; [82] (*b*) diffusion of sodium chloride in agar-agar gels; [83] (*c*) coagulation of pectin; [84] (*d*) gels of calcium hydrate [85] and of titanic; [86] (*e*) rubber gels; [87] (*f*) adsorption of acids and alkalis by agar gels.[88] The mineral content of the agar is an important factor, especially in the acid adsorption.

An interesting paper by E. H. Callow [89] deals with the velocity of ice crystallisation through supercooled gelatin gels (at $-3°$). Seeding the gels in tubes with ice crystals causes ice to separate down the tubes at a uniform velocity, which is less the more concentrated the gel. Varying the p_H with hydrochloric acid leads to a minimum velocity at the isoelectric point (p_H 4·7) and a maximum at p_H 2·6. Other data refer to the effects of neutral salts, and to salts plus acids, *e.g.*, addition of sodium chloride to gelatin–chloride gels retards the velocity of crystallisation to a marked extent.

Liesegang Rings.

Wo. Ostwald [90] advances a theory of Liesegang rings limited to

[77] *Kolloid-Z.*, 1925, **36**, 222; *A.*, ii, 685.
[78] *Ibid.* (*Zsigmondy Festschr.*), 49; *A.*, ii, 520.
[79] *Ibid.*, p. 202; *A.*, ii, 667.
[80] *Ibid.* (*Zsigmondy Festschr.*), 199.
[81] *J. Amer. Chem. Soc.*, 1925, **47**, 1954; *A.*, ii, 863; compare E. H. Harvey, *Amer. J. Pharm.*, 1925, **97**, 447; *A.*, ii, 965.
[82] H. Neubert, *Koll. Chem. Beihefte*, 1925, **20**, 244; *A.*, ii, 201.
[83] R. Fricke, *Z. Elektrochem.*, 1925, **31**, 430.
[84] W. Kopaczewski, *Bull. Soc. Chim. biol.*, 1925, **7**, 419; *A.*, i, 872.
[85] Justin-Mueller, *Rev. gén. Coll.*, 1925, **3**, 73.
[86] S. Klosky and C. Marzano, *J. Physical Chem.*, 1925, **29**, 1125.
[87] H. Feuchter, *Koll. Chem. Beihefte*, 1925, **20**, 434.
[88] J. Effront, *Compt. rend.*, 1925, **180**, 29; *A.*, ii, 201.
[89] *Proc. Roy. Soc.*, 1925, *A.*, **108**, 307; *A.*, ii, 777.
[90] *Kolloid-Z.*, 1925, **36** (*Zsigmondy Festschr.*), 380; *A.*, ii, 530.

the periodic layers of precipitates in diffusion reactions. His "diffusion-wave theory" is based on two facts: (1) in all reaction systems furnishing typical periodic layers, there exist at least three main diffusion waves. Two run counter to each other, the third results from the union of the first two and advances in both directions; (2) many, probably all, typical periodic precipitates result from systems belonging, in the sense of the mass-action law, to the so-called limited reactions, *i.e.*, in contrast to such unilateral reactions as the precipitation of barium sulphate, they are incomplete. In illustration the following reaction is discussed in detail:

$$[\text{Jelly} + MgCl_2] + 2NH_4OH \rightleftharpoons Mg(OH)_2 \downarrow + 2NH_4Cl.$$

Initially the diffusion wave of the external electrolyte (ammonium hydroxide) into the gel is checked by the formation of magnesium hydroxide, the concentration of ammonium hydroxide thus being reduced. The diffusion wave of the internal electrolyte (magnesium chloride) advances towards the region of low concentration of ammonia. Meanwhile the electrolyte ammonium chloride sets up a pronounced diffusion wave in opposite directions from a region of maximum concentration. A condition is reached where the concentrations of ammonium hydroxide and magnesium chloride are so small and that of ammonium chloride so great, that no further precipitation of magnesium hydroxide can be formed in that region. Experimental evidence supports the theory, as, for instance, the fact that rhythmic precipitates dissolve in excess of the reaction electrolyte. Again, if the latter is previously added to the gel, the resulting strata change in width and in the distance separating them.

N. R. Dhar and A. C. Chatterji [91] have extended their work relating to Liesegang rings. Their theory is that peptisation and coagulation are essential factors in ring formation, the rings being due to coagulation of the peptised substance. The coagulum then adsorbs the same material from its surroundings, thus leaving clear zones. Two classes of Liesegang rings are postulated. In one the precipitated layer is followed by a clear layer free from the reactants causing the precipitate, adsorption of the sol having occurred. In the other class the precipitated layer is followed by a clear zone containing non-adsorbed peptised substance. The authors discuss many previous investigations by other workers in this field and interpret their results according to the present theory, which is capable of explaining the majority.

K. Popp [92] has investigated in considerable detail the periodic

[91] *Kolloid-Z.*, 1925, **37**, 2, 89; *A.*, ii, 865, 959.
[92] *Ibid.*, 1925, **36**, 208; *A.*, ii, 667.

precipitation of the system: $MgCl_2 + 2NH_4OH \rightleftharpoons Mg(OH)_2 + 2NH_4HCl$. The order of the reactants used has no appreciable influence on the results, which entirely support Ostwald's wave-diffusion theory. The results are conveniently summarised as follows:—

	Decrease in				
Rings.	$MgCl_2$.	NH_4OH.	NH_4Cl.	Gelatin.	Temperature.
Number.	Increase.	Decrease.	Increase.	Constant.	Slower formation.
Width.	Increase.	Decrease.	Increase.	Increase.	Increase.
Distance between.	Decrease.	Increase.	Decrease.	Increase.	Increase.

P. P. von Weimarn's [93] view of the problem is that periodic rings can result in so many different ways that a single point of view cannot explain them all. He believes a fundamental factor is the periodic alteration in the concentration of protective colloid and disperse phase caused by the precipitate-forming reactants meeting.

Periodic strata in dilute gelatin gels, with silver nitrate and potassium dichromate as reactants, are influenced by the age of the gel and by illumination. Most interesting results were obtained by G. W. Scott-Blair.[94] The distance to the last Liesegang ring increased as the gel aged up to ten days, but with further ageing no strata formed. The facts seem to be connected with a change in the gel structure. Light of various wave-lengths influences the periodicity of the layers to different extents, the effect being irreversible, since if the gel is melted and allowed to re-set, the irregular periodicity of layers persists. Fundamentally distinct from this is the action of ultra-violet light, which after a few hours' irradiation so affects the gel that rings will not form; melting and re-setting now permits the normal Liesegang phenomenon.

W. M. Fischer [95] bases a theory of the formation of rhythmic precipitation in gels on the variation of the time of precipitation from saturated solutions of salts of different valencies. U-Shaped bands in gelatin gels are described by G. V. Stuckert [96] and a new Liesegang pattern formed by coloured salts in solid gels has been studied by E. R. Riegel and L. Widgoff.[97]

Rhythmic crystallisation of sodium sulphate in thin agar-agar films is influenced by several factors, light increasing the rate and too rapid drying causing irregularities. The gel must have a low

[93] *Kolloid-Z.*, 1925, **37**, 78; *A.*, ii, 959.
[94] *Phil. Mag.*, 1925, **49**, 90; *A.*, ii, 519.
[95] *Z. anorg. Chem.*, 1925, **145**, 311; *A.*, ii, 853.
[96] *Kolloid-Z.*, 1925, **37**, 238; *A.*, ii, 1061.
[97] *J. Physical Chem.*, 1925, **29**, 872; *A.*, ii, 863.

agar-agar content, and the salt solution should commence dilute (0·25*M*).[98]

Proteins.

A. Blanche-tière [99] has reviewed the evolution of our knowledge of the chemical structure of proteins. An extensive paper by W. F. Hoffman and R. A. Gortner [1] gives the results of several years' work on proteins and the results in places radically disagree with Loeb. The paper is too long for summary here, but the following quotation regarding the isoelectric point is of interest. "The measured isoelectric 'point' of a protein probably is not a definite point but should in all probability be referred to as an isoelectric range. The position of this isoelectric range on the p_H scale is dependent on the chemical composition of the protein. The calculated isoelectric point is very near the hydrogen-ion concentration of neutral water. This is what would be predicted on the theory that at the higher concentrations of acid and alkali the binding of acid and alkali follows the adsorption law. The calculated isoelectric points are not related to the chemical composition of the protein."

I. M. Kolthoff [2] believes that the albumins are distinct chemical individuals, their amphoteric character being due to the presence of free amino- and carboxyl groups, and not to the group ·CO·NH·. H. R. Kruyt [3] states his reasons for believing the solutions of albumin to be true colloid systems.

As pointed out by S. P. L. Sörensen, an important question in colloid chemistry is how far it is possible to apply to protein solutions the theories derived from the study of real solutions. In a paper [4] on the solubility of proteins he records observations on the precipitation of several proteins and the conditions of their solubility in water and salt solutions. It is shown that the behaviour of albumins when precipitated with ammonium salts does not exclude the application of the phase rule in its usual form and with its usual consequences. This probably extends to other protein precipitations.

Electrolyte-free, water-soluble proteins (glutin, serum-albumin, and ovalbumin) have been obtained by F. Modern and W. Pauli [5] by dialysis followed by electrodialysis. The same authors have

[98] F. O. Anderegg and G. W. Daubenspeck, *Proc. Indiana Acad. Sci.*, 1925, **34**, 171.

[99] *Bull. Soc. Chim. biol.*, 1925, **7**, 218.

[1] Second Colloid Symposium, 1925, 209; *A.*, i, 1479. A further paper appears in *J. Physical Chem.*, 1925, **29**, 760; *A.*, ii, 1011.

[2] *Chem. Weekblad*, 1925, **22**, 489; *A.*, ii, 1055.

[3] *Ibid.*, 473; *A.*, ii, 1056.

[4] *J. Amer. Chem. Soc.*, 1925, **47**, 457; *A.*, i, 602.

[5] *Biochem. Z.*, 1925, **156**, 482; *A.*, ii, 518.

shown [6] that electrolyte-free blood-albumin and egg-albumin form chlorides with hydrochloric acid, at the same time giving positive and negative protein ions due to a hitherto unrecognised combination of hydrochloric acid with amphoteric ions.

The isoelectric points for gliadin and glutenin have been determined by E. L. Tague [7] as p_H 6·5 and p_H 7·0, respectively.

Several papers deal with the molecular weight of proteins. L. J. Harris [8] finds the equivalent combining weight of a protein by adding successive amounts of acid or alkali to the protein and observing a physical constant of the solution which follows. A curve relating this constant to the acid or alkali added will have a sharp discontinuity at that point corresponding to the addition of a constant equivalent of acid or alkali. From similar considerations, E. J. Cohn, J. L. Hendry and A. M. Prenbiss [9] have determined the minimal molecular weight of proteins: gelatin 10,300, zein 19,400, gliadin 20,700, egg-albumin 33,800, serum-albumin 45,000, casein 192,000. Several other values are also given. From surface tension measurements of very dilute egg-albumin solutions, P. L. du Noüy [10] calculates the upper limit for the molecular weight as 30,800. Further, he finds it probable that the dimensions of the space occupied by one molecule of crystalline egg-albumin are 30·9 × 30·8 × 41·7 Å.U.

A review of the coagulation of proteins by heat has been presented by M. Sörensen and S. P. L. Sörensen.[11] Decomposition does not accompany such denaturation, unless the heating with hot water is continued. Water is always lost by egg-albumin when denaturation occurs, but it is not known whether this loss is a constant. The conclusion reached by H. Wu and D. Y. Wu [12] is that denaturation of egg-albumin by heat, acid, or alkali is undoubtedly a hydrolytic process. Exceptional was horse-serum-albumin which, on heating in 0·05 *N*-hydrochloric acid, was not denatured.

When globulin is heated in water at 100°, its subsequent solubility in alkali is reduced to 20%, in hydrochloric acid to 2·5%, and in neutral salt solutions to 1% of that of the original protein. M. Adolf [13] discusses in considerable detail the changes so produced by heating globulin.

[6] *Anal. Asoc. Quím. Argentina*, 1925, **23**, 93.
[7] *J. Amer. Chem. Soc.*, 1925, **47**, 418; *A.*, ii, 391.
[8] *Proc. Roy. Soc.*, 1925, *B*, **97**, 364; *A.*, i, 450.
[9] *J. Biol. Chem.*, 1925, **63**, 721.
[10] *Ibid.*, 1925, **64**, 595; *A.*, ii, 939.
[11] *Compt. rend. Trav. Lab. Carlsberg*, 1925, **15**, 1.
[12] *J. Biol. Chem.*, 1925, **64**, 369; *A.*, i, 1110.
[13] *Koll. Chem. Beihefte*, 1925, **20**, 288; *A.*, ii, 199.

In the precipitation of albumin by salts there is an "irregular series" or "tolerance zone." The first zone of precipitation is obtained with very dilute heavy-metal solutions, the zone of no precipitation (tolerance zone) being obtained with increasing concentration of heavy-metal salt. A second zone of precipitation has been shown to be due to denaturing of the albumin. A. W. Thomas and E. R. Norris,[14] who have investigated this problem, find the first precipitation zone depends on the p_H of the solution and the tolerance zone is due to the passage of the solution from the alkaline to the acid side of the isoelectric point of the protein.

Several workers have dealt with casein. According to M. Fischenich and M. Pólányi,[15] casein ion takes no part in the conductivity of casein solutions. Experiments on the solubility of casein in hydrochloric acid and in mixtures of phosphoric acid and sodium phosphate lead to the conclusion that casein is a mixture of different substances. Results of Loeb and of Pauli relating to the osmotic pressure, membrane potential, viscosity, and electrical conductivity in alkaline caseinate solutions have been confirmed by K. Kondo.[16]

G. S. Adair [17] has determined the osmotic pressures of solutions of various hæmoglobins by a direct method. Rapid equilibrium is attained by a special osmometer and measurements are made at 0°. H. C. Wilson [18] discusses the increase in osmotic pressure which results when hæmoglobin is dialysed in an osmometer against acetic acid, basing his explanation on Donnan's theory of membrane equilibrium.

An important paper on membrane equilibrium has been contributed by E. Hückel.[19] This treatment is largely mathematical and concerns an exact thermodynamic theory of membrane equilibrium for ideal and real solutions of completely dissociated electrolytes. The Debye theory of electrolytes is applied to the membrane equilibrium of the strong electrolytes and is confirmed by the data of Donnan and Allmand on the system potassium ferrocyanide–potassium chloride.

F. Chodat [20] has applied Donnan's theory of membrane equilibrium to the swelling of gelatin in weak acids. N. Kameyama [21] discusses Donnan and Allmand's results on the membrane equilibrium of potassium chloride against potassium ferrocyanide, from

[14] *J. Amer. Chem. Soc.*, 1925, **47**, 501; *A.*, i, 603.
[15] *Kolloid-Z.*, 1925, **36**, 278; *A.*, ii, 662.
[16] *Compt. rend. Trav. Lab. Carlsberg*, 1925, **15**, 39; *A.*, ii, 518.
[17] *Proc. Roy. Soc.*, 1925, *A.*, **108**, 627; *A.*, ii, 965.
[18] *Biochem. J.*, 1925, **19**, 80; *A.*, ii, 292.
[19] *Kolloid-Z.*, 1925, **36** (*Zsigmondy Festschr.*), 204; *A.*, ii, 528.
[20] *Bull. Soc. Chim. biol.*, 1925, **7**, 113; *A.*, ii, 521.
[21] *Phil. Mag.*, 1925, **50**, 849; *A.*, ii, 1062.

the point of view of the newer concepts of activity coefficients, and finds good agreement.

A good review of the modern work on proteins and the Donnan equilibrium has been given by D. L. Hitchcock.[22] The same author[23] has investigated the adsorption of protein from solutions by collodion discs. The adsorption is a maximum at the isoelectric point.

Soaps.

Several important papers have appeared from the Bristol laboratory. McBain[24] in his Royal Institution lecture on "Soaps and the Theory of Colloids" surveys the work of his laboratory, finally pointing out that the behaviour of the highly complex mixtures of saponified oils and fats with various electrolytes met with in soap-boiling can be treated largely on the simple basis of a three-component system. Phase-rule models may be employed to follow and predict quantitatively all the soap-boiling processes. Such a complete survey has, for the first time, been made of the stable systems of water, soap and sodium chloride.[25] Observations are recorded upon equilibria in nearly 200 systems containing pure sodium palmitate, water, and sodium chloride over a range of temperature up to 200° (in sealed tubes). The behaviour of the system is apparently independent of time. Summarising their work, McBain and Langdon state that in any soap system, whether prepared from a commercial oil or pure soap, the following phases exist: true lamellar crystals, crystalline curd fibres, anisotropic liquid "neat soap," anisotropic liquid "middle soap" (existence previously unsuspected), isotropic liquid. All the soap-boiling operations depend on equilibria between these phases. "The limits of the field of existence of isotropic liquid solutions of sodium palmitate, with and without salt, have been accurately determined for temperatures up to 150°. This single phase includes wholly crystalloidal and wholly colloidal solutions and ranges at sufficiently high temperatures from pure water up to pure anhydrous liquid sodium palmitate, the two being miscible in all proportions above 316°."

W. C. Quick[26] confirms previous work showing that the ionic micelle in soap systems is a hydrated colloidal aggregate of simple fatty ions. In a solution which is weight normal with regard to potassium chloride and potassium laurate, accurate determinations were made of the transport of each of the constituents during

[22] *Physiol. Rev.*, 1925, **4**, 505.
[23] *J. Gen. Physiol.*, 1925, **8**, 61; *A.*, ii, 1054.
[24] *Proc. Roy. Inst. Gt. Britain*, March 20 (1925), 6 pp.
[25] J. W. McBain and G. M. Langdon, *J.*, 1925, **127**, 852.
[26] *Ibid.*, p. 1401.

electrolysis. The quantities of potassium, laurate, and chloride ions transported were 0·47, 0·19, and 0·32 equivalent, respectively. Only three-fifths of the total current is carried by potassium chloride, the remaining two-fifths by the ionic micelle. It was shown that the hydration of potassium laurate in N_w-solution, where it is entirely neutral (neutral colloid and ionic micelle), amounts to 12·8 mols. of water per equivalent of laurate, this confirming the value found by McBain and Jenkins by the wholly independent ultrafiltration method (*J.*, 1922, **121**, 2325).

Miss M. E. Laing [27] summarises the work of several investigators at Bristol on the unstable states of solutions of sodium behenate. At room temperature a 0·05—0·5 N_w-sodium behenate solution is a hard white curd. By special heat-treatment curd formation is temporarily suspended, clear, very mobile liquids ensuing, characterised by marked hydrolysis. The largest constituent of the unstable mobile solutions is neutral undissociated soap, the next largest being colloidal acid sodium soap with the equivalent quantity of free sodium hydroxide. There is only about 5% of dissociated soap.

The constitution of the system sodium stearate–water has been investigated by A. von Buzagh,[28] who infers that the water in soap gels is held mechanically. Ultrafiltration yields a liquid with a conductivity less than that of the original solution and it is suggested that this is due to adsorption of stearate molecules by stearic acid resulting from hydrolysis.

Experiments by W. A. Patrick, W. L. Hyden, and E. F. Milau [29] show that sodium oleate in ethyl-alcoholic solution is a simple electrolyte, being highly ionised at the boiling point in the case of dilute solutions. Even at high concentrations dissociation occurs. A small amount of water has little, if any, effect upon the dissociation.

The change in degree of dispersion of soap solutions when treated with uni- and bi-valent metal chlorides is ascribed by R. Minakami [30] to ionic antagonism. The coarse-grained structure due to addition of lithium chloride changes to a fine-grained structure when small amounts of magnesium chloride are added.

The viscosity of aqueous soap solutions has attracted several workers. N. A. Jajnik and K. S. Malik [31] used solutions of pure sodium palmitate and stearate, finding that the viscosity varies directly as the concentration and inversely as the temperature

[27] *J.*, 1925, **127**, 2751.
[28] *Chem. Zentr.*, 1925, **96**, II, 271.
[29] *J. Physical Chem.*, 1925, **29**, 1004.
[30] *Biochem. Z.*, 1925, **158**, 306; *A.*, ii, 860.
[31] *Kolloid-Z.*, 1925, **36**, 322; *A.*, ii, 779.

The palmitate has the lesser viscosity, but as the concentration and temperature decrease the viscosities of the two soap solutions approach each other; $N/20$- and $N/24$-solutions at 60° have almost identical viscosities. The results are held to support the view of McBain on the constitution of soap solutions. From the work of H. Freundlich and H. J. Kores [32] on the viscosity of soap solutions it is concluded that solutions of sodium oleate show no elasticity, whilst solutions of sodium stearate only do so in concentrated solutions. Mixed dilute solutions of these two soaps show a pronounced elasticity. The ultramicroscope revealed long threads in the mixed solutions, although the initial separate solutions did not contain them. The threads probably represent a mesomorphous phase. Commenting on this investigation, E. Hatschek [33] draws attention to the considerable elasticity shown by even dilute solutions of ammonium oleate.

In connexion with the *X*-ray examination of soaps as thin films on various metal supports, J. J. Trillat [34] shows that the affinity between a metal and fatty acids to form soaps may be gauged by a study of the spectrum intensity produced. The analysis of soap films according to Miss M. E. Laing's experiments on bubbles from sodium oleate solutions, shows the presence of acid sodium soap and not free oleic acid.[35]

Another attempt to standardise a method for comparing the detergent efficiencies of soaps is based on the observation that when dilute soap solutions are shaken with powdered flake graphite in presence of air, the appearance of a white band at the lower boundary of the froth indicates the presence of an excess of soap. The graphite is standardised against an ammonium palmitate solution containing sufficient excess of ammonia to insure maximum detergent power.[36]

Starch.

Electrolyte-free starch sols have been obtained by M. Samec,[37] by heating to 120° and separating into fractions by electro-dialysis. The different fractions give different colours with iodine and have different gold numbers. The molecular weights vary from 90,000 to 156,000. It is further shown by Samec [38] that the iodine colour of starch sol components is, within wide limits, independent of the

[32] *Kolloid-Z.*, 1925, **36**, 241; *A.*, ii, 663.
[33] *Ibid.*, 1925, **37**, 25; *A.*, ii, 862.
[34] *Compt. rend.*, 1925, **180**, 1838; *A.*, ii, 752.
[35] *Proc. Roy. Soc.*, 1925, *A*, **109**, 28; *A.*, ii, 960.
[36] R. M. Chapin, *J. Ind. Eng. Chem.*, 1925, **17**, 461.
[37] *Compt. rend.*, 1925, **181**, 477; *A.*, ii, 1153.
[38] *Koll. Chem. Beihefte*, 1925, **21**, 55.

mean molecular weight. No simple relation could be found connecting iodine colour and gold number.

H. D. Murray [39] has measured the concentrations of the various substances formed when a solution of iodine in carbon tetrachloride is shaken with an aqueous solution of starch with and without the addition of small quantities of potassium iodide. From his data he suggests that starch iodide is an addition compound, the anion of which, in dilute potassium iodide solutions, has the formula $(C_6H_{10}O_5)_nI'_5$, where n is approximately 15. From his work on the influence of adsorption on the colour of precipitates, N. R. Dhar [40] infers that it is probable that the blue colour of adsorption compounds of iodine with starch, dextrin, cholalic acid, and basic lanthanum acetate is due to the existence of iodine in the colloidal condition in such compounds.

A paper by S. M. Neale [41] deals with the elasticity and tensile strength of starch films, their general behaviour resembling that of a ductile metal.

Capillarity.

The thermodynamics of capillary action have been discussed by L. Gay,[42] who derives the thermodynamic laws of capillarity and investigates the restrictions on the phase rule in systems where capillary forces are propounded. Using the equation $W = T_{LV}(1 + \cos\theta)$, where W = adhesion, or work done in separating a solid from a liquid, T_{LV} = free surface energy (surface tension) at the liquid–vapour boundary, θ = angle of contact, N. K. Adam and G. Jessop [43] have investigated the angles of contact and the polarity of solid surfaces. Since W measures the adhesion of solid and liquid, and $2T_{LV}$ the cohesion of the liquid, the equation shows that when $\theta = 0°$ the solid–liquid attraction is at least as great as the liquid–liquid attraction; $\theta = 180°$ indicates no solid–liquid attraction, whilst $\theta = 90°$ shows this adhesion to be half that of the liquid cohesion. From this point of view determinations of θ against water give a quantitative guide to the polarity of a solid surface. The authors "attempted to use the values of W for solid surfaces of long-chain aliphatic compounds as an indication of the orientation of the surface molecules. If many polar groups are at the free surface, the angle of contact should be low; if the surface consists solely of the hydrocarbon ends of the chain, the angle should be approximately the same as for paraffin wax." An angle of about

[39] *J.*, 1925, **127**, 1288.
[40] *J. Physical Chem.*, 1925, **29**, 1394.
[41] *J. Text. Inst.*, 1925, **15**, T, 443; *A.*, ii, 783.
[42] *J. Chim. Phys.*, 1925, **22**, 116.
[43] *J.*, 1925, **127**, 1863.

100° was found for paraffin wax, whether solidified in air or water, or scraped in air; similarly for octadecyl iodide. The nine substances used give results explicable on the authors' theory. In an extension of this work,[44] the " blooming " of varnish films is treated as an indication of polarity, and the above method compared with the catalytic activity method of Norrish (*J.*, 1923, **123**, 3006). The attractions for water parallel the veiling properties of the varnishes; if the attraction of water for varnish exceeds 70% of that of water for itself, veiling occurs, but there is no veiling when the attraction is less than 45—50%.

E. K. Carver and F. Hovorka[45] have determined the capillary rise of water and benzene in capillary tubes of glass, copper, silver, and zinc and found the height to be the same in each case, a result contradicting the earlier work of Bigelow and Hunter (*J. Physical Chem.*, 1911, **15**, 367).

Interesting work has been carried out by J. G. Popesco[46] relating to the capillary properties of mercury. Mercury was formed as drops in a vacuum and in various gases (O, N, H, CO_2, CO, NH_3). The surface tension of mercury in a vacuum was determined as 436·3 dynes/cm. When mercury drops formed in a vacuum are exposed to gases, the surface tension is less than in a vacuum, and decreases (towards a limit) with time. Mercury, as drops made in a gas, has a surface tension greater than in a vacuum, but the value decreases until in about 24 hours a constant value is reached, lower than in a vacuum. Ultra-violet illumination of a negatively charged mercury drop in a vacuum causes a reduction in surface tension. The results are discussed on the theory of adsorption-orientation (Langmuir, Frenkel, and Harkins).

The electrocapillarity of mercury as influenced by colloids forms the subject of an important paper by K. Šandera.[47] Kučera's dropping-mercury electrode method was used (*Ann. Physik*, 1903, **11**, 529, 698). The surface tension of the dropping-mercury cathode (interface solution/mercury) is greatly influenced by the concentration and the capillary-activity of added colloids, even small amounts (*e.g.*, 0·001% gelatin, 0·01% glycogen, 0·05% gum arabic) of capillary-active colloids sufficing to displace the maximum of the electro-capillary curve. Arsenious sulphide sol requires a minimum concentration of 0·5%, ferrous hydroxide sol 0·1%. Generalising, positive colloids displace the maximum of the electrocapillary curve to the more negative polarising potential, negative colloids to the

[44] N. K. Adam, R. S. Morrell, and R. G. W. Norrish, *ibid.*, p. 2793.
[45] *J. Amer. Chem. Soc.*, 1925, **47**, 1325; *A.*, ii, 647.
[46] *Ann. Physique*, 1925, **3**, 402; *A.*, ii, 952.
[47] *Rec. trav. chim.*, 1925, **44**, 480—7; *A.*, ii, 659.

positively polarising potential. The results are discussed in connexion with adsorption, Helmholz layer, and adsorption potential.

K. Schultze [48] has investigated the connexion between capillarity and evaporation and efflorescence. For true (circular) capillaries the evaporation of water is independent of the cross-sectional area, but is greater the nearer the meniscus approaches the end of the capillary. As the distance between the meniscus and the end increases, the evaporation rapidly slows down. The slope of the capillary is without influence provided there is no change in the position of the meniscus. In the case of "mixed" capillaries (irregular cross-section) evaporation depends on the cross-section and the form of the meniscus. Such conditions are present in evaporation from granular and porous materials. The work has been extended to a consideration of the relation between capillarity and wetting.[49]

The extent to which surface forces influence the wetting of yarn during sizing is examined by F. D. Farrow and S. M. Neale,[50] their data including surface tensions of solutions of starches, sodium oleate, *cyclo*hexanol, and Turkey-red oil, as well as interfacial tension of these solutions against paraffin and castor oil.

W. Bachmann and C. Brieger [51] find a connexion between the heat of wetting of lubricating oils and metal (pure copper). The better lubricating oils had the higher heats of wetting, and in agreement with this is the observation that a small addition of unsaturated acid such as oleic, to a petroleum oil produced a relatively large increase in the heat of wetting. Such a mixture has been found by Southcombe and Wells (*J. Soc. Chem. Ind.*, 1920, **39**, 51T) to have enhanced lubricating efficiency.

W. Kopaczewski [52] has investigated the electrocapillary analysis of natural and synthetic dye sols using strips of filter-paper. Electronegative dyes ascend to the same height as water, colouring the upper edge of the paper more deeply, whilst electropositive dyes rise but little, staining being pronounced at the liquid contact. Amphoteric dyes form bands of light and deep colour, whilst colloids of low surface tension show good ascension independent of the electric charge.

Surface Tension.

Considerations based on the Eötvös expression $(dA/dT)V_m^{2/3} =$ constant, where A = capillary constant of a liquid, V_m = molecular

[48] *Kolloid-Z.*, 1925, **36**, 65—78.
[49] *Kolloid-Z.*, 1925, **37**, 10.
[50] *J. Text. Inst.*, 1925, **16**, 209 T.
[51] *Kolloid-Z.*, 1925, **36** (*Zsigmondy Festschr.*), 142; *A.*, ii, 510.
ompt. rend., 1925, **180**, 1530; *A.*, ii, 828.

volume, have led Brillouin [53] to the conclusion that the molecules in the surface layer of a liquid are about as far apart as are the molecules in the interior of the liquid. The molecular significance of surface tension has been discussed by N. K. Adam and G. Jessop [54] on the basis of experiments on the development of streamers at the interface of two liquids during mixing. Very interesting work has been carried out on a large number of liquids by C. V. Raman and L. A. Ramdas [55] relating to the connexion between the scattering of light at liquid surfaces and surface tension. Lowering of the surface tension, or increase in refractive index, is accompanied by a more intense surface opalescence. Thus, when oleic acid spreads on water in quantity just sufficient to prevent camphor movements, the surface opalescence is about twice as great. Addition of further oleic acid results in an enormous increase in surface films. In this case, a discontinuous surface results, due to minute globules of oleic acid.

S. Sugden [56] has dealt with the mathematics underlying the determination of the surface tension of a liquid by the method of rise in capillary tubes.

When water drops into the saturated vapours of carbon tetrachloride, light petroleum, toluene, benzene, chloroform, triethylamine, and ethyl ether, the surface activity of these vapours influences the surface tension of the water to an extent parallel with the interfacial activity of the corresponding organic liquids on water.[57] The effect of capillary-active substances on the surface tension of salt solutions has been investigated by W. Seith.[58] Solutions of methyl, *iso*propyl, *iso*butyl, and *iso*amyl alcohols, and of aniline, in pure water at various concentrations were treated with solutions of salts such as the chlorides of sodium, potassium, lithium, magnesium, and barium, also magnesium sulphate and urea, and the surface tensions determined by the method of Stocker (*Z. physikal. Chem.*, 1920, **94**, 149). The surface tension lowering due to the presence of the capillary-active alcohols is intensified by the presence of the salts, the effect increasing with the salt concentration. Curves relating surface tension to quantity of capillary-active solute give, for the systems containing different concentrations of salts, a family of curves cutting in one point. Ionic hydration is considered the underlying cause of the salt effect. The degree

[53] *Compt. rend.*, 1925, **180**, 1248; *A.*, ii, 496.
[54] *Proc. Roy. Soc.*, 1925, *A*, **108**, 324; *A.*, ii, 772.
[55] *Ibid.*, **109**, 150, 272; *A.*, ii, 952, 1046.
[56] *J. Amer. Chem. Soc.*, 1925, **47**, 60.
[57] V. Korán, *Rec. trav. chim.*, 1925, **44**, 460; *A.*, ii, 659.
[58] *Z. physikal. Chem.*, 1925, **117**, 257; *A.*, ii, 961.

of hydration of the ions may be calculated from the lowering of surface tension produced.

R. G. Schulz [59] deals with the distribution of surface-active substances between water and organic solvents, and W. D. Harkins and H. M. McLaughlin [60] consider unimolecular film formation between liquids. The number and disposition of molecules in unit area are considered from the standpoint of molecular dimensions and the theory of orientation.

The lowest surface tension so far found for a dilute aqueous solution is that of 0·1 *M*-sodium nonoate, the value being 20·2 dynes/cm. at 20°. Addition of sodium hydroxide sufficient to make this solution 0·005 *M* with respect to the base increases the surface tension to 45·4 dynes/cm., and at 0·008 *M* to 48·8 dynes/cm. Thereafter additions of sodium hydroxide decrease the surface tension linearly. The explanation given [61] is that the extremely low surface tension is due to a surface film of sodium nonoate and nonoic acid resulting from hydrolysis. Sodium hydroxide, by repressing hydrolysis, raises the surface tension due to removal of the acid, further sodium hydroxide then increasing the activity of sodium nonoate in the solution and also its concentration in the film, thereby lowering surface tension.

The surface tensions of the two liquid phases formed by water and phenol at different temperatures have been determined by A. K. Goard and E. K. Rideal.[62] The difference between the surface tensions of the two phases diminishes regularly up to the critical solution temperature, and no "inversion point" at 40° to 45° was found. Greater miscibility of the liquids is accompanied by a decreasing difference in the surface tension of the phases. It was found that the phase richer in the low-tension component had the higher surface tension. For determining the interfacial tension between two liquids, P. L. du Noüy [63] recommends the well-known platinum ring tensimeter, the tension being measured directly in dynes from the force required to drag the ring from the dineric interface.

Wo. Ostwald and A. Steiner [64] have published an interesting paper on the inter-connexion of surface tension and frothing capacity. Low surface tension of a liquid is, of itself, not sufficient to confer the capacity to foam. Liquids of quite high surface

[59] *Koll. Chem. Beihefte*, 1925, **21**, 37; *A.*, ii, 956.
[60] *J. Amer. Chem. Soc.*, 1925, **47**, 1610; *A.*, ii, 771.
[61] W. D. Harkins and G. L. Clark, *ibid.*, p. 1854; *A.*, ii, 857.
[62] *J.*, 1925, **127**, 780.
[63] *Compt. rend.*, 1925, **180**, 1579; *A.*, ii, 647.
[64] *Kolloid-Z.*, 1925, **36**, 342; *A.*, ii, 771.

tension can foam, and in some cases reduction of surface tension can destroy foaming.

Useful data relating the surface tension of wort and beers to the colloid constituents and p_H values have been presented by G. T. Peard and J. H. St. Johnston,[65] their work bearing directly on the problem of frothing. A similar communication is due to J. King.[66]

Interface Phenomena.

Of the many phases of colloid research one of the most important theoretically, and one which is attracting increasing attention, concerns the phenomena of concentration gradient at interfaces, chiefly the air–liquid interface. Numerous papers have appeared during the year dealing with surface concentration, molecular structure of surface films, orientation, and surface energy.

A general discussion from the point of view of thermodynamics deals with the effect of surface energy on colloidal equilibrium.[67] The free energy of a surface is considered to consist of that energy covered by the ordinary concept of surface tension and also a certain free energy due to a potential difference between the surface of a particle and the surrounding liquid. The discussion deals with changes in surfaces in relation to area only, not to thickness or density. Two interesting reviews deal with "Chemistry at Interfaces" (W. B. Hardy)[68] and "The Structure of Surface Films on Water" (N. K. Adam).[69]

The Gibbs adsorption equation has been deduced thermodynamically by M. Volmer,[70] whilst A. Frumkin[71] gives a simple method for the proof of the Gibbs equation. Addition in drops of solution of lauric acid in light petroleum to water causes the surface tension of the water to decrease as the ether evaporates. As soon as the surface layer is "saturated" with lauric acid a further drop of etheral solution but slowly disappears. The time required to reach this condition is definite and reproducible. Frumkin in this way found the "saturation capacity" of the water surface to be $5{\cdot}2 \times 10^{-10}$ mol. of lauric acid per sq. cm. Now connecting the surface tension depression of water containing lauric acid in solution with concentration, the quantity $-d\sigma/d \log C$ may be calculated graphically. Frumkin found for this quantity 13·9, whence Gibbs's

[65] *J. Inst. Brewing*, 1925, **31**, 416.
[66] *Ibid.*, p. 32.
[67] H. O. Halvorson and R. G. Green, Second Colloid Symposium, 1925, 185.
[68] *J.*, 1925, **127**, 1207.
[69] *J. Physical Chem.*, 1925, **29**, 87; *A.*, ii, 195.
[70] *Z. physikal. Chem.*, 1925, **115**, 253; *A.*, ii, 539.
[71] *Ibid.*, 1925, **116**, 498; *A.*, ii, 856.

equation, $-(1/RT)d\sigma/d \log C$, gives $5{\cdot}7 \times 10^{-10}$ mol. of lauric acid per sq. cm. The agreement in the two results is excellent.

Frumkin [72] has also considered the distribution of a substance between two phases, connecting the partition coefficient with the work done in transferring one mole of the substance from one phase to the other. His considerations when applied to the distribution between internal liquid and surface layer, lead to Traube's rule for the increase in adsorbability in homologous series.

A comprehensive review of work concerning the *P.D.*'s and electrical charges arising at a liquid–gas interface has been published by H. W. Gilbert and P. E. Shaw,[73] who add a bibliography. The electrical properties of unimolecular films of adsorbed insoluble substances have been investigated by A. Frumkin,[74] who measured the *P.D.* at the interface air–adsorbed film. The observed effects in the case of the higher members of homologous series can be explained on the basis of Langmuir's orientation theories, but the effect per mole is less than in the case of the lower members of the series.

R. K. Schofield and E. K. Rideal [75] have examined the surface tension–concentration curves for aqueous solution of several capillary-active organic substances. It is believed that the molecules of these capillary-active substances are adsorbed from a dilute solution in a unimolecular layer and "that the effect they produce on the surface tension is due to their thermal agitation alone. At a given temperature their effectiveness depends solely on their surface concentration, their interfacial areas and their lateral cohesion." A critical examination is made of Traube's views on surface tension in relation to osmotic pressure, and a modified equation is reached: $F(A - B) = xRT$, analogous to that of Amagat connecting the pressure and volume of highly compressed gases. Here F = surface tension, A = area occupied by a gram-mole of the active substance at the interface, B = limiting area of a gram-mole under high compression, and $1/x$ = measure of the lateral molecular cohesion. The equation accords with data for water–air, water–benzene, and water–mercury interfaces.

A. Cary and E. K. Rideal [76] have dealt in three papers with the behaviour of crystals and lenses of fat on the surface of water. "In an experimental study of the process of surface spreading on water and solutions of 0·01 *N*-hydrochloric acid of organic compounds containing a long chain terminating in a polar group,

[72] *Z. physikal. Chem.*, 1925, **116**, 501; *A.*, ii, 856.
[73] *Proc. Phys. Soc.* (London), 1925, **37**, 195; *A.*, ii, 795.
[74] *Z. physikal. Chem.*, 1925, **116**, 485; *A.*, ii, 873.
[75] *Proc. Roy. Soc.*, 1925, *A*, **109**, 57; *A.*, ii, 960.
[76] *Ibid.*, pp. 301, 318, 331; *A.*, ii, 1046, 1047, 1048.

including acids, esters, ethers, phenols and nitriles, it is found that unimolecular films spread from crystals as well as lenses, a definite equilibrium surface tension or two-dimensional pressure characteristic of the substance in question being established." When an oil film spreads, this is due to the pushing effect of incoming molecules (from the lens or crystal) rather than the attractive pull of the uncontaminated water. The second paper deals with the effect of temperature on the pressure of a film in equilibrium with a crystal or lens of various organic long-chain compounds ending in polar groups. Highly insoluble solid compounds do not affect the surface tension of water below a certain definite temperature, above which, until the melting point is reached, surface tension decreases linearly with temperature rise. A sudden change in the slope of the curve occurs at the melting point, but the linear relation continues to hold. Exceptions were noted and an explanation was advanced. The third communication concerns the effect of the polar group on the equilibrium pressure. Although further experimental work is necessary, it seems that the slope of the surface-tension curve up to the melting point is determined by the hydrocarbon chain, and thereafter the polar group is the important factor.

From very accurate measurements of the surface tensions of sodium chloride solutions from 0·1 to 5*M*, W. D. Harkins and H. M. McLaughlin [77] deduce that the apparent thickness of the water film on a solution of sodium chloride is 4 Å.U. at a concentration of 0·1 *M*, falling to 2·3 Å.U. at 5*M*. The thickness is, therefore, of the order of a linear dimension of a water molecule and it is suggested that the ions in the solutions "keep buried beneath a monomolecular film of water. As the concentration of salt increases, the diffusion pressure forces the ions closer and closer to the surface."

Several papers deal with unimolecular films in various connexions, prominent being those by P. L. du Noüy,[78] J. F. Carrière,[79] and W. D. Harkins and J. W. Morgan.[80] Studies of surface concentration comprise several contributions. J. M. Johlin [81] determined the surface tension of ash-free isoelectric gelatin at 40° at the air–liquid boundary for various concentrations of aqueous solution, the change in surface tension being noted with the increasing age of the interface. The change in surface tension with time takes place according to the equation $\sigma = a/t^n$, where σ = surface tension,

[77] *J. Amer. Chem. Soc.*, 1925, **47**, 2083; *A.*, ii, 959.
[78] *J. Phys. Radium*, 1925, **6**, 145; *A.*, ii, 844; *J. Expt. Med.*, 1925, **41**, 663.
[79] *Rec. trav. chim.*, 1925, **44**, 121; *A.*, ii, 287.
[80] *Proc. Nat. Acad. Sci.*, 1925, **11**, 637; *A.*, ii, 1148.
[81] *J. Physical Chem.*, 1925, **29**, 271, 1129; *A.*, ii, 388, 1054.

t = time, a and n constants. The relation holds well for dilute solutions over a considerable period of time. Johlin found the equation also valid in the case of sodium oleate solutions of 1 to 0·0001% concentration. It also held for colloidal sulphur, and no satisfactory explanation is as yet advanced as to why this should be so. The same equation expresses the rate of surface concentration of casein, crystalline egg-albumin, and crystalline hæmoglobin.[82]

E. Keiser [83] finds that cholesterol and its esters decrease the surface tension of water. The surface activity of the esters falls off as the number of carbon atoms in the acids increases. J. B. Leathes [84] produces striking photographic evidence for the orientation of molecules at the interface between cholesterol and water (and aqueous solutions).

An important paper by A. Frumkin [85] gives the surface tension curves of the higher fatty acids together with an equation for the condition of the surface layer. The curves relate to solutions of caprylic, caproic and lauric acids, Wilhemy's method being used. It is shown that the deviation in form of the curves from those shown by the lower fatty acids is explicable on the effect of attractive forces and (finally) condensation phenomena in the adsorbed layer. The equation of Szyszkowski (*Z. physikal. Chem.*, 1908, **64**, 385) may be modified to include a term depending on the mutual attraction of the adsorbed molecules, and it will then satisfy the observed data.

A. K. Goard and E. K. Rideal [86] raise the interesting question as to whether the presence of a unimolecular adsorbed film of oriented (phenol) molecules at a water surface solely determines the surface tension. Their results indicate that molecules at greater depths also have an influence upon it. "A complete theory of surface tension should cover both the surface film and the 'foundation' upon which that film rests."

Adsorption.

A general review of the theories of adsorption is given in a paper by L. Abonnenc.[87] The various adsorption equations proposed by Langmuir, A. M. Williams, Freundlich and others have been discussed by A. Gorbatschev,[88] his investigations dealing with the density of the lines of force at the adsorbing surface.

[82] *Loc. cit.*, p. 897.
[83] *Biochem. Z.*, 1925, **154**, 321.
[84] *The Lancet*, 1925, 853, 958, 1019.
[85] *Z. physikal. Chem.*, 1925, **116**, 466; *A.*, ii, 856.
[86] *J.*, 1925, **127**, 1668.
[87] *Rev. gén. Sci.*, 1925, **36**, 262.
[88] *Z. physikal. Chem.*, 1925, **117**, 129; *A.*, ii, 959.

Wo. Ostwald and H. Schulze [89] have shown that the adsorption curve obtained when $(C_0 - C)$ is plotted against C has an S-form if the curve includes $C = 0$ and $C = 100$. Here C_0 = initial percentage of solute in solution, and C = percentage of solute in solution when adsorption is complete. Simultaneous adsorption of solvent as well as solute must be accounted for. The paper is an important contribution to adsorption problems and should be read in conjunction with another discussion on the S-curve, given by K. W. Flörov.[90] M. Pólányi [91] has derived an equation connecting adsorption with swelling pressure and osmotic pressure. It is argued by B. Iljin [92] that adsorption is not a specific phenomenon. Assuming a purely electrical origin for adsorption forces, he derives an equation connecting the heat of adsorption and adsorption capacity with the dielectric constant and surface energy of the adsorbent.[93]

Adsorption from Gases.—W. D. Bancroft [94] has written a general discussion of the work done by various investigators on electrification in relation to the removal of adsorbed gas films. An experimental investigation of the dynamical equation of the process of gas adsorption was undertaken by D. H. Bangham and W. Sever,[95] who confirm the equation of $d \log s/d \log t$ = constant $(1/m)$ for the early stages of the process of sorption on glass surfaces. Here s = quantity of gas adsorbed in time t. For time–sorption data beyond the range of obedience to the first equation, the equation $\log \sigma/(\sigma - s) = kt^{1/m}$ holds, σ being the limiting values of s as t approaches infinity.

B. Iljin [96] derives formulæ for calculating the extent of adsorbing surfaces. Three different methods give the adsorbing surface of 1 gram of charcoal as being of the order 10^5 sq. cm. It is proved that for equal values of the heat of adsorption the quantities of gas adsorbed per sq. cm. of different surfaces (carbon and mica) are the same. The surface energy of an adsorbent is a measure of its adsorption activity.

W. A. Patrick and his collaborators have published several important papers on adsorption. Previous work by Patrick on the relation of capillarity to adsorption is reviewed, particularly in relation to silica gel experiments.[97] Accurate measurements have been made

[89] *Kolloid-Z.*, 1925, **36**, 289; *A.*, ii, 657. [90] *Ibid.*, p. 215; *A.*, ii, 657.
[91] *Z. physikal. Chem.*, 1925, **114**, 387; *A.*, ii, 290.
[92] *Z. Physik*, 1925, **33**, 435; *A.*, ii, 958; *Physikal. Z.*, 1925, **14**, 497
[93] *Phil. Mag.*, 1925, [vi], **50**, 1144; *A.*, ii, 1149.
[94] *J. Physical Chem.*, 1925, **29**, 20.
[95] *Phil. Mag.*, 1925, [vi], **49**, 935; *A.*, ii, 507.
[96] *Z. physikal. Chem.*, 1925, **116**, 431; *A.*, ii, 856.
[97] *Kolloid-Z.*, 1925, **36** (*Zsigmondy Festschr.*), 272; *A.*, ii, 509.

of the adsorption of carbon dioxide and nitrous oxide by silica gel at 0°, 20°, 30°, and 40°, at pressures below one atmosphere.[98] The results point to the fact that the liquid in the capillaries at temperatures near the critical temperature exhibits an increase in surface tension due to capillary forces. The critical temperature is raised in the pores of the adsorbent. In another investigation,[99] a dynamic method was used to follow the adsorption of vapours of alcohol, carbon tetrachloride, benzene, and water by silica gel. With the exception of water, excellent agreement was found with the equation $V = K(P\sigma/P_0)^{1/n}$, based on the capillary theory of adsorption. Here P = the partial pressure at equilibrium of the vapour adsorbed, P_0 = the saturation pressure at the temperature, σ = surface tension, V = c.c. of vapour adsorbed per gram of gel. K and $1/n$ are constants depending only on the gel structure. Water shows anomalous behaviour due to increased viscosity of the adsorbed water, the internal pressure having been decreased by capillary and surface tension forces. Further support of the capillary adsorption theory is given by data concerning the adsorption of butane by silica gel.[1]

Patrick and C. E. Greider [2] have measured the heats of adsorption of sulphur dioxide and water vapour by silica gel at 0°. In each case the difference between the heat of adsorption and the heat of liquefaction is explained on the basis of surface energy considerations. R. C. Ray [3] has determined the adsorption of nitrogen peroxide by silica gel at different temperatures and pressures, Freundlich's empirical equation holds for all the cases investigated. except when the saturation pressures were approached. Within certain limits, the water content of the gel exerts no influence on the amount of adsorption.

Various investigators have employed glass as the adsorbing surface. D'Huart [4] studied the adsorption of water vapour, alcohol, chloroform, benzene and toluene vapours. The water adsorbed varies as the surface area of the glass and as the vapour pressure. The organic vapours were adsorbed but to a very small degree. The rate of sorption of ammonia by a glass surface at 0° was measured at various pressures by D. H. Bangham and F. P. Burt.[5] The results at all pressures and times over the experimental range accorded with the equation $s^m = kp_t\int_0^t p \, . \, dt$, where s = the sorption value at time t, p_t = the momentary pressure, and m is

[98] *J. Physical Chem.*, 1925, **29**, 421; *A.*, ii, 508.
[99] W. A. Patrick and L. H. Opdycke, *ibid.*, p. 601; *A.*, ii, 656.
[1] W. A. Patrick and J. S. Long, *ibid.*, p. 336; *A.*, ii, 382.
[2] *Ibid.*, p. 1031. [3] *Ibid.*, p. 74.
[4] *Compt. rend.*, 1925, **180**, 1594; *A.*, ii, 657.
[5] *J. Physical Chem.*, 1925, **29**, 113; *A.*, ii, 284.

approximately constant (about 12). In the case of carbon dioxide, analogous results were obtained, but m varied with the pressure, to which the sorption value was much more sensitive. "While for strictly constant pressure experiments with ammonia it was concluded that logs would be a (nearly) linear function of $\log(p^2t)$, for carbon dioxide, under the same conditions, $\log s$ would be a (non-linear) function of $\log(p^5t)$." Similar work has been done by these authors, using nitrous oxide and sulphur dioxide.[6]

E. Moles and R. Miravalles [7] believe that in the adsorption of hydriodic acid by glass, capillary condensation may occur, and that in addition to true adsorption chemical reaction between the acid and glass can take place. I. R. McHaffie and S. Lenher [8] studied the films of water adsorbed from the gas phase on plane glass and platinum surfaces when the pressure of the water vapour was near the saturation value. Their method directly measures the number of molecules adsorbed from a saturated vapour on a known area of a plane surface. The adsorption was calculated from measurements of the decrease in pressure in the system when passing from temperatures at which all the water present was in the gas state (and at pressures proportional to the absolute temperature) to temperatures where the entire mass of water was in the vapour state (and the pressures equalled the vapour pressure of the water at the corresponding temperature). Adsorption began at a finite pressure and was reversible. The glass adsorbed much more than did platinum. The adsorbed film varied from 0 to $5{\cdot}3 \times 10^{-6}$ cm. in thickness for glass, and 0 to $1{\cdot}13 \times 10^{-6}$ cm. for platinum.

Numerous papers deal with charcoal as an adsorbent for gases. The whole subject is reviewed by I. L. Abonnenc.[9] The question of the adsorptive power of charcoal in relation to activation is considered by H. Herbst,[10] O. Ruff and E. Hohlfeld,[11] F. König [12] and H. H. Lowry and S. O. Morgan.[13] The difference between the adsorptive power of charcoal before and after compression has been dealt with by E. Urbain,[14] who goes into the question of porosity in relation to gas adsorption. Hydrogen activates graphite as a sorbent for oxygen, but has no influence on the adsorption for carbon dioxide.[15]

[6] D. H. Bangham and E. P. Burt, *ibid.*, p. 540; *A.*, ii, 657.
[7] *Anal. Fis. Quim.*, 1925, **23**, 223. [8] *J.*, 1925, **127**, 1559.
[9] *Rev. gén. Sci.*, 1925, **36**. See also W. Mecklenburg, *Z. angew. Chem.*, 1925, **37**, 873. [10] *Koll. Chem. Beihefte*, 1925, **21**, 1.
[11] *Kolloid-Z.*, 1925, **36**, 23; *A.*, ii, 192.
[12] *Pharm. Zentr.*, 1925, **66**, 645; *A.*, ii, 1054.
[13] *J. Physical Chem.*, 1925, **29**, 1105.
[14] *Compt. rend.*, 1925, **180**, 63; *A.*, ii, 191.
[15] D. H. Bangham and J. Stafford, *J.*, 1925, **127**, 1085.

The use of charcoal in gas-masks to adsorb poisonous gases from air has been dealt with by W. Mecklenburg [16] in an important paper. The general problem of the adsorption equilibria of mixtures of two gases is of great interest. R. Lorenz and E. Wiedbrauck [17] used charcoal, adsorbing from mixtures of carbon dioxide and hydrogen. As the carbon dioxide in the initial gas phase is increased, the time required for establishing equilibrium decreases, but the amount of gas required to saturate the charcoal increases. Carbon dioxide is adsorbed more easily than is hydrogen, temperature has but little effect. Other mixtures which gave very interesting results were carbon dioxide–carbon monoxide and carbon dioxide–ethylene.

Other adsorbents investigated in relation to gas adsorption are silica gel,[18] alumina,[19] titania,[20] and cellulose nitrate.[21] B. Foresti,[22] measuring the heat of adsorption of hydrogen on nickel, cannot confirm the results obtained by Beebe and Taylor (*J. Amer. Chem. Soc.*, 1924, **46**, 43).

Adsorption from Solution.—It has been shown by H. L. Richardson and P. W. Robertson [23] that adsorption from solution may be determined by a cryoscopic method. The adsorption of any substance soluble in the chosen solvent may be determined from its freezing-point depression curves, it being a simple matter to follow the rate of change of adsorption with concentration. Adsorption from various systems by means of carbon and silica gel lead E. Berl and E. Wachendorff [24] to the conclusion that an important factor in adsorption is the lyophobe and lyophile character of the adsorbent, and that the behaviour of the latter with the solvent requires consideration. With a given adsorbent and different liquids, the capacity for adsorbing solutes is the more pronounced the smaller the heat of wetting of the adsorbent.

W. A. Patrick and D. C. Jones [25] believe "that adsorption by silica gel is due to a phase separation in the capillaries caused by preferential wetting followed by the production of highly concave surfaces of solute which brings about a lowering of the solubility of the solute in the solvent." A study of the adsorption of water

[16] *Z. Elektrochem.*, 1925, **31**, 488.
[17] *Z. anorg. Chem.*, 1925, **143**, 268; *A.*, ii, 382.
[18] H. A. Fells and J. B. Firth, *J. Physical Chem.*, 1925, **29**, 241.
[19] J. H. Berry, *ibid.*, p. 1462; L. A. Munroe and F. M. G. Johnson, *J. Ind. Eng. Chem.*, 1925, 88.
[20] F. Bischoff and H. Adkins, *J. Amer. Chem. Soc.*, 1925, **47**, 807.
[21] D. Costa, *Gazzetta*, 1925, **55**, 540; *A.*, ii, 956.
[22] *Ibid.*, p. 185.
[23] *J.*, 1925, **127**, 553.
[24] *Kolloid-Z.*, 1925, **36** (*Zsigmondy Festschr.*), 36; *A.*, ii, 507.
[25] *J. Physical Chem.*, 1925, **29**, 1; *A.*, ii, 193.

from *n*-butyl alcohol by silica gel leads Patrick and N. F. Eberman [26] to the conclusion that a liquid in a capillary has a greater surface tension than the bulk liquid under the same conditions, the difference being greater the higher the temperature. As the dispersity of silica gel is increased, the adsorption forces increase but in a greater proportion. The adsorption is only due in part to increase in specific surface, the main effect depending on the increased proximity of the solid surfaces, the radii of the capillaries so produced being less than the range of the attractive forces causing adsorption. The upper limit for the thickness of the adsorbed layer on silica gel is about 5 molecules, the data being calculated from the adsorption of nitrobenzene in kerosene solution.

W. A. Patrick and E. H. Barclay [27] divide adsorption phenomena into 3 classes : (*a*) chemical adsorption, (*b*) molecular adsorption, (*c*) capillary adsorption. "Chemical adsorption would include all cases where attractive forces between the adsorbent and adsorbed substance were so strong as to be equal to real chemical attractive forces."

An extensive paper by J. N. Mukherjee [28] concerns the nature of hydrolytic adsorption, *i.e.*, cases where acids or alkalis are liberated by the interaction between solutions of salts having a neutral reaction and insoluble substances which do not give an acid or alkaline extract with water. Hydrolytic adsorption is explained on the author's theory of the distribution of ions in the Helmholtz electric double layer (*Phil. Mag.*, 1922, **44**, 330, 340).

An interesting investigation by J. S. Beekley and H. S. Taylor [29] deals with the adsorption of silver salts by silver iodide, this having a definite known crystal-lattice even in the spongy precipitate in which form it was used. Univalent silver salts were chosen so as to eliminate the factors of varying electric charge and valence. The adsorption of silver salts followed the order : benzoate > acetate > nitrite > bromate > naphthalenesulphonate > benzenesulphonate > nitrate > chlorate > ethylsulphate > perchlorate. In general, the less soluble salts are the more strongly adsorbed. The results agree with certain theoretical deductions concerning the factors influencing the attraction of silver ions from solution by the crystal surface. Thus, great affinity of the anion in solution for the silver ion (as manifested by high solubility) means lessened attraction by the crystal and therefore less adsorption.

The use of charcoal as adsorbent is indicated in several papers, and a review of the chief properties of the more important technical

[26] *J. Physical Chem.*, 1925, **29**, p. 220; *A.*, ii, 284.
[27] *Ibid.*, p. 1400. [28] *J. Indian Chem. Soc.*, 1925, **2**, 191.
[29] *J. Physical Chem.*, 1925, **29**, 942; *A.*, ii, 855.

active charcoals has been given by H. Herbst.[30] Impregnation of active charcoal with a dry, indifferent salt decreases the purely static adsorption capacity in direct proportion to the salt content, but the adsorption velocity falls off more quickly. At 80% salt, the adsorption velocity in relation to that of the initial active charcoal is nil. To determine the efficiency of a charcoal as adsorbent, E. Dingemanse and E. Laqueur[31] find the methylene-blue adsorbent test very satisfactory.

The question of the adsorption efficiency of charcoal in viscous media is of interest. The work of G. Weissenberger and H. Waldmann[32] on the adsorption by various charcoals of iodine from aqueous glycerol solutions and several organic solutions shows that Freundlich's concentration function holds in all cases. The adsorption, x/m, increases as the viscosity decreases, but not in direct proportion, the relation being $x/m = \beta/\eta^{1/r}$ where η = viscosity and β and $^{1}/_{r}$ = constants.

E. J. Miller,[33] dealing with the adsorption of hydrogen and hydroxyl ions by activated sugar charcoal, finds that acids are adsorbed whereas alkalis such as potassium hydroxide are negatively adsorbed. His results lead him to the conclusion that the Harkins-Langmuir orientation theory is applicable to the interface charcoal–solution. In another paper the idea is advanced that "the adsorbed molecules of solute are oriented at the solid–liquid interface, the more polar portion being on the solution side." For aqueous solutions, the introduction of polar groups into a solute decreases its adsorption by charcoal.[34]

WILLIAM CLAYTON.

[30] *Koll. Chem. Beihefte*, 1925, **21**, 1; *A.*, ii, 956.
[31] *Biochem. Z.*, 1925, **160**, 407; *A.*, i, 1500.
[32] *Monatsh.*, 1925, **45**, 393.
[33] *J. Amer. Chem. Soc.*, 1925, **47**, 1270; *A.*, ii, 656.
[34] F. E. Bartell and E. J. Miller, *J. Physical Chem.*, 1925, **29**, 982.

PHOTOCHEMISTRY, 1914–1925

Synopsis.

I. *Introductory.*
- (i) Preliminary.
- (ii) New Inorganic Photochemical Reactions.
- (iii) Photochemistry of Chlorine.

II. *General.*
- (i) Absorption Spectrum and Photosensitivity Spectrum.
- (ii) Intensity and Velocity.
- (iii) Concentration and Velocity.
- (iv) Absorbed Light and Velocity.
- (v) Temperature and Velocity.
- (vi) Photosensitisers and Photocatalysts.
- (vii) Negative Photocatalysts and Inhibitors.
- (viii) Solvent and Velocity.
- (ix) Photochemical Stationary States.
- (x) Photochemical Extinction.
- (xi) Photochemical Induction.
- (xii) After-effects in Photochemical Reactions.
- (xiii) Analogies between Photochemical and Other Types of Chemical Change.

III. *Energetics.*
- (i) Thermodynamics and Photochemistry.
- (ii) Radiation Theory of Chemical Kinetics and Photochemistry.
- (iii) The Photochemical Equivalent Law.

IV. *Mechanism of Photochemical Change.*
- (i) Preliminary.
- (ii) The Primary Process.
  - (*a*) Dissociation.
  - (*b*) Activation.
  - (*c*) Life of Activated Molecules.
- (iii) Fate of Activated Molecules.
  - (*a*) Deactivation by Radiation.
  - (*b*) Deactivation by Collision.
  - (*c*) Collisions with Acceptors.
  - (*d*) Reaction Chains.
  - (*e*) Effect of Water Vapour.

I. *Introductory.*

(i) *Preliminary.*

In choosing the last twelve years as the period to be covered by this Report, the Reporter has been guided by two considerations. First, the commencement of the period roughly coincides with a considerably increased interest in the subject, due to the introduction by Einstein [1] of the quantum theory into photochemistry under the form of the Photochemical Equivalent Law. The out-

break of the War certainly effectively disguised this increased interest as far as the output of actual published work was concerned. But 1914 rather than 1919 nevertheless seems the more logical starting year to choose. Secondly, an excellent progress report, covering the transition years 1909–1913, was published in 1914 by Winther.[2] This afforded a starting-point of another kind, and the present Report may, in that sense, be regarded as a continuation of that of Winther.

Limitations of space primarily, but also other reasons, have decided the Reporter to omit consideration, except incidentally, of certain important aspects of the subject. These are—the photochemistry of the photographic emulsion and of solid systems generally; photosynthesis in its usual special significance; therapeutic and other practical applications of light action which fall within, or border on, the field of photochemistry; photogalvanic phenomena; photo-reactions in organic chemistry, except where quantitatively worked out; phototropy; technique of quantitative work. These subjects would either demand for adequate treatment more space than is available, or have been fully discussed recently, or are in too early a stage of development to justify discussion. It is believed that these omissions will give the Report a more homogeneous character than would have been possible otherwise.

(ii) *New Inorganic Photochemical Reactions.*

Comparatively few, new, purely inorganic reactions have been discovered. Cario and Franck[3] have shown that molecular hydrogen at low pressures can be dissociated to atoms if insolated in presence of mercury vapour by light of wave-length 254 μμ. If mixtures of hydrogen and certain reducible gases at ordinary pressures are similarly insolated in presence of mercury by a lamp rich in the same radiation, rapid interaction takes place.[4] Amongst other gases, nitrous oxide is reduced to water and nitrogen. Moore and W. A. Noyes, jun.,[5] have shown that oxygen reacts with mercury to form traces of mercuric oxide in the light of the quartz-mercury lamp, even if the light is cut off just before the admission of oxygen, whilst the reaction between mercury and nitrogen peroxide is accelerated. According to Noyes,[6] quartz-mercury light, from which rays of shorter wave-length than 215 μμ have been filtered out, will cause nitrogen and hydrogen in presence of boiling mercury to form ammonia up to about the thermodynamic equilibrium concentration. Warburg has studied the ozonisation of liquid oxygen.[7] Winther[8] has shown that oxygen can be ozonised in presence of zinc oxide by irradiation with light of wave-lengths

which would have no action on oxygen alone. The zinc oxide is unchanged. The mutual reaction between ozone and hydrogen peroxide solutions is much accelerated in light.[9] The photo-decomposition of gaseous chlorine dioxide was shown by Bowen [10] to give an unstable, reddish-brown liquid. The subject was followed up by Booth and Bowen [11] and by Bodenstein, Harteck, and Padelt.[12] The latter workers showed the liquid to be Cl_2O_6. It can also be formed by irradiation of a mixture of ozone and chlorine with red light, which is absorbed by, and activates, the ozone.

A number of new organic substitution and addition photo-reactions in which the halogens take part have been discovered, but will not be enumerated here. It may, however, be mentioned that the combination of carbon monoxide and oxygen [13] and the decomposition of sulphuryl chloride [14] and of chlorine monoxide [15] must be added to the list of reactions which are sensitised for visible light by chlorine. Bonhoeffer [16] has shown that the decomposition of carbonyl bromide and of ozone will take place in blue light in the presence of bromine. Winther [17] has shown the oxidation of hydriodic acid solutions by oxygen to iodine to be sensitised for blue light by I_3^- ions first formed by a dark reaction, and has pointed to other previously known reactions as being examples of such *auto-sensitisation*. von Strachoff [18] draws the same general conclusion. Trautz [19] has demonstrated the photochemical union of carbon monoxide and bromine. Noddack [20] and Grüss [21] have studied the chlorination of trichlorobromomethane dissolved in carbon or silicon tetrachloride, and Grüss [21] has shown that, in presence of bromine and in carbon tetrachloride solution, blue light can cause the oxidation of trichlorobromomethane by oxygen to carbonyl chloride. von Goldberger [22] has demonstrated that carbonyl chloride is reduced by hydrogen in ultra-violet light, carbon monoxide and hydrogen chloride being the chief products.

Dhar [23] has shown that a number of reactions that proceed with appreciable velocities in the dark are materially accelerated by light. Such are the reduction of iodine, bromine, and other oxidising agents by various organic acids and their salts; the reduction of iodine by nitrites and by ferrous salts, etc. The equilibrium $2Fe^{++} + I_3^- \rightleftarrows 2Fe^{+++} + 3I^-$ is moved to the right when the solution is insolated [24] by yellow light.[25] The slow decomposition of aqueous solutions of alkali metal perchlorates, periodates, and iodates by light from a powerful quartz-mercury lamp is noted by Oertel [26] (that of bromates and chlorates had already been recorded [27]). Matthews and Curtis [28] have shown that mixtures of potassium iodide with either the chlorate, bromate, or iodate undergo comparatively rapid decomposition in these circumstances, with liber-

ation of iodine. According to Mukerji and Dhar,[29] sunlight accelerates the decomposition of nitrous acid solutions. The photodecomposition of nitrogen pentoxide is sensitised for blue light by the presence of the peroxide.[30] Norrish and Rideal [31] have shown that light of wave-length about 275 $\mu\mu$ causes the union of hydrogen and sulphur vapour at 300—340°, and Benrath [32] records the photoreduction of aqueous solutions of sulphur dioxide, and of the oxyacids of selenium and tellurium, to the free element by oxalic acid. Sulphuryl chloride can be decomposed by light of a suitable wavelength.[14, 19] The reaction is a complex one. According to Baur,[33] pure solutions of potassium ferrocyanide are not acted on by light, the photosensitivity of ordinary solutions being due to the presence of ferricyanide.

The great majority of photo-reactions in which the electropositive constituent of a metallic compound is the active photochemical agent are photo-oxidations of organic substances (chiefly aliphatic alcohols, hydroxy-acids and dicarboxylic acids), the inorganic compound either being reduced to a lower stage of oxidation or acting as a carrier for oxygen. Many have been noted for the first time during the period under review, and, in particular, the photochemical properties of some of the rarer metallic compounds have been investigated. The results, however, are of the usual type, and need no further notice. One curious reaction deserves mention—that between zinc oxide and an aqueous silver nitrate solution in sunlight. Following up the work of others, Baur and Perret [34] showed that, whilst the final result of the reaction is essentially the production of metallic silver, oxygen, and zinc nitrate, an unstable peroxide of silver (probably Ag_2O_3) is formed as an intermediate product of the reaction.

(iii) *Photochemistry of Chlorine.*

The last twelve years have been marked by intensive work, much of it quantitative, directed towards the elucidation of the mechanism of already known reactions. Chlorine still remains the photochemical element of mystery, and the majority of papers published on the photo-reactions of this element still note some striking new experimental results or conclusions—not always, it is true, subsequently confirmed. The following is a summary of papers on the photochemistry of chlorine which have appeared since the beginning of 1914 :

Combination with hydrogen. From the laboratory of Jesus College, Oxford, have come experimental papers by D. L. Chapman and Whiston,[35] and by M. C. C. Chapman,[36] the first two dealing chiefly with the effect of concentration and the third with that of light

intensity. The latter subject has also been studied by Baly and Barker.[37] Weigert and Kellermann [38] have investigated the initial stages of the reaction by new experimental methods. Coehn and his collaborators [39] have studied the effect on the reaction of the addition of traces of water vapour to the thoroughly dried gases. Marshall, after showing that the introduction of hydrogen atoms into a hydrogen–chlorine mixture in the dark caused formation of hydrogen chloride,[40] investigated the photochemical reaction from the point of view of quantum efficiency over a large range of pressure.[41] Experiments of this nature promise to be of great value. Quantum efficiency measurements have also been made by Kornfeld and Müller.[42] Padoa and Butironi [43] have studied the temperature coefficient in light of various wave-lengths, whilst Coehn and Jung [39d] and W. Taylor [44] have published work on the effect of wave-length on velocity. Padoa and Butironi found the reaction to go with light of wave-length 530—550 μμ, Coehn and Jung conclude that 540 μμ is the limiting wave-length which will bring about the change, whilst Taylor gives 490 μμ, the limit of the continuous absorption band of chlorine, as the same critical wave-length. Bowen [45] has criticised these conclusions of Taylor and of Coehn and Jung. Finally, inhibition phenomena due to the presence of ammonia have been investigated by Norrish.[46] Theoretical papers on the mechanism of the reaction have been published by Bodenstein,[47] Göhring,[48] D. L. Chapman and M. C. C. Chapman,[49] Berthoud,[50] and Cathala.[51]

Combination with carbon monoxide. This reaction has been worked on by Bodenstein,[13] Bonhoeffer,[16] Cathala,[52] and Coehn and Tramm.[39a, b] These last authors, and also Bodenstein, found the reaction to be much retarded if the gases were exhaustively dried.

Combination with sulphur dioxide. This reaction has been studied by Trautz,[19] Le Blanc,[14] Bonhoeffer,[16] and by Coehn and Tramm.[39a,b]

Combination with ozone. In red light, Cl_2O_6 can result.[12]

Substitution reactions. The chlorination of methane has been worked on by Whiston,[53] of solutions of trichlorobromomethane by Noddack [20] and by Grüss,[21] of toluene at — 80° by Book and Eggert,[54] and of solutions of various aliphatic compounds in carbon tetrachloride by Benrath and Hertel.[55]

Reactions sensitised by gaseous chlorine. Work has been done on the decomposition of sulphuryl chloride,[14] ozone,[16] and chlorine monoxide,[15] the union of carbon monoxide and oxygen,[13] and the synthesis of water.[56]

Reactions in aqueous solution. The photo-decomposition of chlorine water has been studied under various conditions by Mil-

bauer,[57] Benrath and Tuchel,[58] Benrath, Schaffganz, and Oberbach,[59] and by Allmand, Cunliffe, and Maddison.[60] Anderson and H. S. Taylor [61] report that a solution of hydrogen peroxide containing a small amount of chlorine decomposes very rapidly in ultra-violet light.

Miscellaneous reactions. Nasaroff [62] has worked on the kinetics of the addition of chlorine to cinnamic acid in carbon tetrachloride solution. According to Plotnikov,[63] solutions of chlorine in carbon tetrachloride, exposed to light, undergo a periodic variation in titre. Grüss [21] and Benrath and Hertel [55] state, on the other hand, that perfectly pure carbon tetrachloride is not an acceptor for chlorine. Plotnikov [64] nevertheless does not hesitate to assert the real existence of periodic reactions as a new type of photochemical change.

Action of light on, and activation of, chlorine. In view of the remarkable photochemical properties of the element, attempts continue to be made to " activate " it in the absence of an acceptor. Le Blanc and Volmer [65] and Bodenstein and H. S. Taylor [66] have brought hydrogen into contact with chlorine within an interval of 1/1000—1/1500 second after the light had been cut off from the latter, but without any hydrogen chloride formation. Similar fruitless experiments were made by Wendt, Landauer, and Ewing.[67] On the other hand, these last observers were able to confirm older work in that a pre-insolation of chlorine alone shortens the induction period for a subsequent *photo-reaction* between hydrogen and chlorine. " Activation " of chlorine for subsequent dark reactions is reported by Venkataramaiah [68] and by Schaum and Feller.[69] Venkataramaiah used both electrical discharges and radiation from iron arcs, and claims to have evidence that some sort of a complex molecule is formed.[70] The latter authors used electric discharges only. They, as also Wendt and his co-workers,[67] suggest the formation of Cl_3 as a possibility. Göhring [48] draws the same conclusion from another point of view. Radel [71] and Jones [72] have studied the formation of the clouds produced in moist chlorine or chlorine–air mixtures on insolation, and their results in both cases are of considerable interest. The same phenomenon has been remarked by Weigert and Kellermann.[38b]

Finally may be mentioned a paper by Weigert [73] in which an attempt is made to work out a general mechanism for all gaseous chlorine photo-reactions.

II. *General.*

(i) *Absorption Spectrum and Photosensitivity Spectrum.*

It is, of course, universally recognised that absorption of radiation, not necessarily by the reacting substance, must precede photo-

chemical change. On the other hand, answers to the following queries still remain to be given. Amongst those rays which are absorbed, why are some photochemically active and others not? If a particular wave-length inside an absorption band can cause chemical change, will this also be the case for every other frequency inside the band? Assuming that a certain frequency range can bring about photochemical change, how will the *photosensitivity*, or rate of chemical change for the same *incident* energy (expressed in ergs/cm.^{2}. second), depend on the frequency? Given the quantitative absorption spectrum, the answer to this last question is, of course, directly connected with the rate of chemical change per unit of *absorbed* energy and its dependence on frequency, a subject which has been much worked on in recent years. For the moment, however, we will consider the matter from the point of view set out above.

To account for the marked differences observed between the photochemical effects resulting from absorption in different parts of the spectrum, several workers have postulated the existence of two types of absorption band—photochemical and thermal. Such a distinction was already made by Plotnikov,[74] prior to 1914, and, in a different form, is implicit in Henri and Wurmser's Law of Elementary Photochemical Absorption.[75] Winther and Oxholt-Howe,[76] from their work on photodecomposition of organic ferric salts, conclude that a photosensitive substance consists of two "constituents," one photosensitive and one absorbing purely thermally. The observed absorption curve results from the superposition of the absorption curves for the two "constituents." Tian [9] regards observed absorption curves as complex in the same way. Andrich and Le Blanc,[77] working on the bromination of toluene and of its solutions in different solvents, found that short-wave ultra-violet light caused rapid reaction in cases where the absorption spectrum in that region resembled that of free bromine (photochemical absorption) and little or no action in cases where the absorption curve indicated marked solvation of the bromine (thermal absorption). Coehn and Stuckardt,[78] from work on the decomposition and synthesis of the hydrogen halides, drew conclusions practically identical with those suggested years before by Luther [79]—namely, that photochemical action is connected with the occurrence of steep, well-defined bands, indicating resonance and forced vibrations in the absorbing molecules, whilst broad and ill-defined bands denote thermal absorption. Luther was thinking in terms of the electromagnetic theory of light absorption, but his ideas on the mechanism of degradation of energy during the process of thermal absorption are applicable, with slight changes, when using the theory

of discontinuous absorption. Thus, Warburg, whilst admitting that a change in the *character* of absorption with frequency (and thus a difference in *character* between thermal and photochemical absorption) is possible,[80] if unlikely, suggests [81] that the loss of energy during absorption, by collision of the absorbing molecules with neighbouring molecules, which is regarded as the cause of broad absorption bands and lines, may also be responsible for such absorption resulting in little or no chemical change, but in the production of heat. In the case of the continuous absorption bands of chlorine and bromine, Ribaud [82] explains the same energy degradation as due, not to collisions with contiguous gaseous molecules, but to *intra-molecular* perturbation, probably electronic in nature. (Energy degradation of this sort had also been taken into account by Luther.) It may be significant that chlorine and bromine are both photochemically active within these regions. In the case of chlorine, indeed, W. Taylor [44] draws the conclusion that only absorption within the continuous absorption band will photoactivate the gas, and that absorption in the neighbouring region of fine structure bands is without effect. Bowen [45] has pointed out an apparent flaw in his reasoning. In any case, it is certain that the first question posed above can only be answered when we have more exact knowledge of the mechanism of absorption of radiation by molecules. Such knowledge is accumulating fairly quickly [see Section IV (ii)], and in these circumstances, the attempts of Weigert [83] to work out from this point of view the mechanism of light absorption and photochemical change are perhaps somewhat premature.

The question of the threshold or critical frequency necessary for photochemical change has been attacked in several ways, but is still undecided. In the case of the decomposition of sulphur dioxide to sulphur trioxide and sulphur, Hill [84] concludes that, within the sulphur dioxide absorption band, any frequency will decompose the gas, provided that the intensity is sufficient. Plotnikov's [74] idea that only a small range of frequency near the long wave-length limit of the band is active, is shown not to hold by Andrich and Le Blanc [77] in the case of the bromination of toluene, and is indeed refuted by many other examples. A number of attempts have been made to calculate the lowest critical frequency which will cause reaction from considerations based on the quantum theory. Their validity is, however, very doubtful. For example, the heat of dissociation of a single molecule has been equated to the magnitude of a quantum (which gives the limiting frequency) by Bowen [85] in the case of the formation and decomposition of the hydrogen halides, by Bowen and Sharp [86] in the case of the dissociation of nitrosyl

chloride, and by Coehn and Jung [39d] for the formation of hydrogen chloride. Volmar [87] has made similar thermochemical calculations of the limiting frequency required for the photolyses of certain aliphatic derivatives, and Job and Emschwiller [88] have used the critical frequency in the decomposition of ethyl iodide to make calculations of the same type. Bowen, in his later papers,[45, 89] now declares that there are no grounds for expecting such relations to exist. This is the view of Franck.[90] Rideal and Williams [25] find that the minimum frequency required to effect the photo-oxidation of Fe^{++} ions by iodine (579 μμ) corresponds to the resonance potential of iodine molecules (2·34 ± 0·2 volts). Finally, attempts to calculate the limiting frequency by equating the corresponding quantum, in accordance with the well-known radiation theory of W. C. McC. Lewis and of Perrin, with the molecular heat of activation, as calculated from the temperature coefficient of the thermal reaction, have not been uniformly successful. Daniels and Johnston [30] did not find nitrogen pentoxide photosensitive at 1·16 μ, as the theory predicted, whilst what at first appeared to be an excellent confirmation in the case of the photo-depolymerisation of dianthracene [91] has recently been shown to be fallacious.[92] The calculations by Hill [84] of the wave-length required for sulphur dioxide decomposition do not carry conviction, nor does the extent of agreement with the theory found by W. A. Noyes, jun., and Kouperman [93] in connexion with oxalic acid decomposition. On the other hand, Griffith and Shutt [94] found ozone to be photosensitive at about 700 μμ as forecasted, whilst Norrish and Rideal consider that the predictions of the theory have been confirmed in the case of the photochemical union of hydrogen and sulphur.[31]

With regard to the observed dependence of photosensitivity on frequency inside a given band, practically all the data published indicate that it increases with frequency. Such data include the work of Boll [95] on the hydrolysis of the chloroplatinic acids, of Spencer [96] on the photolysis of sodium hypochlorite solutions, of Winther and Oxholt-Howe [76] on the decomposition of the ferric salts of organic acids, of Tian [97] on the decomposition of hydrogen peroxide solutions, and of W. Taylor [44] on the combination of hydrogen and chlorine. Berthelot [98] once again states his views on the analogy between frequency in photochemical reactions and temperature in thermal reactions—an analogy in the light of which the experimental facts appear normal. Weigert [83b] has pointed out that, if the Einstein Law [see Section III (iii)] holds, the photosensitivity–wave-length curve should be similar to the absorption curve, but displaced unsymmetrically towards the red. This displacement has long been known to occur in certain reactions,[79b]

and the considerable sensitivity to the red of iodine–potassium oxalate mixtures reported by Berthoud and Bellenot [99] may perhaps be noted in this connexion.

Mention should finally be made of new experiments comparing the action of complex light with the sum total of the action produced by the component bands or rays. Previous to 1914, Luther and Forbes [100] had found these to be equal for the oxidation of quinine by chromic acid, whilst Plotnikov [74] had obtained considerably greater reaction, in the case of the addition of bromine to cinnamic acid, from the summed effects of the single rays, than when using the complex beam. Padoa,[101] reinvestigating this reaction, obtains qualitative confirmation of Plotnikov's results, whilst finding considerable complications owing to the existence of induction periods. The results depend on the order in which the different strips of the spectrum are allowed to act on the solution. The same type of result was got for the decomposition of Eder's solution, and for the ferric chloride–oxalic acid and the hydriodic acid–oxygen reactions.[102] On the other hand, for the hydrogen–chlorine reaction, the yield in white light much exceeded that given by the summed reactions of the different parts of the spectrum.[101] The significance of these data cannot yet be discussed with advantage. Attention may, however, be directed to some probably relevant results of Kuhn,[103] who found the quantum efficiency for ammonia decomposition to decrease with increasing monochromatism of the ultra-violet light used.

(ii) *Intensity and Velocity.*

This has been investigated in comparatively few cases. The methods used for altering the light intensity differ considerably—interposition of a number of sheets of tissue paper of known extinction, of various forms of diaphragms of known fractional aperture or of crossed Nicol prisms; change in slit width when working with dispersed monochromatic light; variation of distance between light source and reaction vessel; a rotating sector. The use of the last device seems to the Reporter to be open to an obvious objection if the object of the experiment is to discover the form of the functional relation between velocity and intensity—it is, on the other hand, well adapted for the investigation of true induction processes or of dark reactions superposed on primary light reactions. Proportionality between intensity and velocity has been found in the cases of the hydrolysis of the chloroplatinic acids,[95] the decomposition of hydrogen peroxide solutions and also of water to hydrogen peroxide and hydrogen,[9] the decomposition of potassium cobalti-oxalate solutions,[104] and for the initial stages of the photolysis of

uranyl formate solutions.[105] In the last case, the extreme intensities used were in the ratio of about 1 : 280. The case of the combination of chlorine and hydrogen is a particularly interesting one. Baly and Barker [37] found that a sixfold increase in the intensity increased the velocity about ten-fold, and Cathala [51] expresses their results by proportionality between $I^{3/2}$ and rate. On the other hand, M. C. C. Chapman [36b] for an intensity ratio of 6 : 1, Marshall [41] for a ratio of 20 : 1, and Kornfeld and Müller [42] for a ratio of 64 : 1, found proportionality between intensity and velocity. In Marshall's experiments, the total pressure was only 5·9 cm. of mercury—all other investigators were using mixtures at about one atmosphere pressure. Berthoud [50] is of opinion that Mrs. Chapman's earlier experiments [36a] suggest that the rate of this reaction may, in circumstances, be proportional to $I^{1/2}$. D. L. Chapman [106] thinks this may be so in complete absence of any inhibitors.

The proposed relation is of much interest, as it would suggest the primary reaction to be the dissociation of chlorine molecules to atoms as the result of their absorption of light, the chlorine atoms then reacting further at a rate proportional to the first power of their concentration. This actually appears to be the type of mechanism in the photosynthesis of hydrogen bromide from its elements, where Bodenstein and Lütkemeyer [107] have shown that the rate of reaction is proportional to the square root of the rate of energy absorption, and therefore presumably to $I^{1/2}$. This relation between velocity and intensity has also been found by Berthoud and Bellenot [99] for the reaction between iodine and potassium oxalate in aqueous solution. Earlier kinetic experiments of Dhar [23d] point to the same result, which has been confirmed recently by Chapman.[106] According to Berthoud,[108] a similar relation holds for the addition of bromine to cinnamic acid, to α-phenylcinnamonitrile, and to stilbene. In the carbon dioxide assimilation reaction, sensitised by chlorophyll, the rate of assimilation increases less rapidly than the intensity.[109] For the photo-oxidation of hydriodic acid to iodine (sensitised by I_3^- ions), Winther, [110] working with monochromatic light of $\lambda = 366$ μμ, obtains the remarkable result that the rate (over a fifty-minute interval) at first increases more or less proportionally with the intensity, and then, comparatively rapidly, becomes independent of any further increase in the latter. Berthoud [108] believes, from Winther's figures, that the $I^{1/2}$ relation holds here also.

One other case has been noted, in which the relation between velocity and intensity is similar to that reported by Baly and Barker [37] for the hydrogen–chlorine reaction, *viz.*, the destruction of certain fluorescing dyes, such as eosin, in aqueous solution by light.

A very rapid disappearance of the fluorescence in intense light was first observed by Perrin.[111] Wood [112] showed that a certain influx of light at high intensity broke down the dye far more extensively than the same amount at low intensity, and this was confirmed by Pringsheim,[113] who also discusses possible explanations of the effect in this and in a subsequent paper.[114]

Our knowledge of the subject of *threshold intensity* remains much as it was. Whereas, on the electromagnetic theory of light absorption, the existence of such a definite effect appeared quite natural, this is not the case when using the quantum theory. Hill [84] indicates the possible presence of such an effect in the decomposition of sulphur dioxide by light of $\lambda = 313$ $\mu\mu$. And the experiments of Dhar and Sanyal [115] on photosynthesis in tropical sunlight may perhaps be interpreted in the same way. But the matter requires careful investigation, with due regard paid to the time factor. Of course, in reactions like the breakdown of the dye solutions referred to above, where the mechanism probably involves collision between two molecules activated by light, a *practical* threshold intensity may well occur.

(iii) *Concentration and Velocity.*

The controversy between the *intensity* and *absorption* formulations of photochemical kinetics was cleared up just before the beginning of the period covered by this Report, and, as is known, in a way which demonstrated that the two conceptions represented extreme cases of a more comprehensive formulation. The introduction of the quantum theory gave a rational theoretical basis to this generalised mode of treatment, whilst the results of experimental work carried out during the last twelve years can, with few exceptions, be satisfactorily fitted into the scheme. With regard to the *concentration of the absorbing substance*, in the great majority of cases the true order of the reaction is one, and the apparent order lies between the limits of zero and one. With complete absorption of the active radiation, it is zero. Such was, for example, the case (or nearly so) in experiments on the decomposition of sulphuryl chloride,[14] of ammonia [103] and of uranyl oxalate solutions,[116] and in the hydrolysis of monochloroacetic acid by water.[117] Cases where the order lies between zero and unity, depending on the thickness of insolated layer, the concentration of the absorbing substance or the extent of the reaction are (absorbing substances mentioned first) the reduction of aromatic ketones [118] or of ammonium dichromate [119] by aliphatic alcohols, and the decomposition of carbon tetrachloride solutions of chlorine monoxide and chlorine dioxide,[120] aqueous solutions of sodium hypochlorite,[96]

formic acid, [121] oxalic acid [122] and uranyl formate,[105] and of nitrosyl chloride [86] and formaldehyde vapour.[22] Reactions found to be of the first order, and probably of the same $0 \longrightarrow 1$ type, were the union of very dry chlorine and carbon monoxide,[13] of sulphur vapour and hydrogen,[31] the decomposition of potassium permanganate solutions,[123] and the reduction of titanium tetrachloride by mandelic acid.[124] Reactions of the second order for the absorbing constituent were found in the cases of the hydrolysis of the chloroplatinic acids,[95] the addition of bromine to α-phenylcinnamonitrile,[125] and the de-ozonisation of ozone–oxygen mixtures.[126] Further, Bodenstein [13] found that the velocity of reaction of ordinarily dried carbon monoxide–chlorine mixtures was of the second order with respect to chlorine. The hydrogen–chlorine reaction also shows discrepant results. Whereas n for chlorine, according to D. L. Chapman and Whiston,[35] is unity (possibly of the $2 \longrightarrow 1$ type), M. C. C. Chapman [36a] finds $n = 1{\cdot}6$, whilst Berthoud [50] would wish to conclude from her results that $n = 1$, and Cathala [51] that $n = 1{\cdot}5$.

There are also two cases in which the observed orders of reaction are difficult to reconcile with the results given by quantum efficiency experiments, *viz.*, the decomposition of solutions of hydrogen peroxide [9, 97, 127] and of potassium cobaltioxalate.[104] Details cannot be gone into, but one would expect in the two cases higher and lower orders, respectively, than those actually found.

Finally, those cases [99, 107] in which the velocity varies as $I^{1/2}$ also give, or tend towards, $n = 0{\cdot}5$ for the reaction order of the absorbing substance.

Sensitised reactions invariably have an order of the $0 \longrightarrow 1$ type for the optical sensitiser. This is the case for the following chlorine-sensitised reactions: ozone [16] and chlorine monoxide [15] decomposition, water synthesis; [46] for the bromine-sensitised transformation of maleic into fumaric ester; [128] for the decomposition of oxalic acid in aqueous solutions sensitised by a low UO_2SO_4 concentration.[95, 122]

The reaction order for *non-absorbing substances* is, with very few exceptions, of the $0 \longrightarrow 1$ type. Examples are numerous, and only those will be referred to in which a change in order was observed accompanying a change in concentration. For example, n for trichlorobromomethane in its reaction with chlorine increases continuously from zero as the mixture is diluted with carbon tetrachloride [20] or silicon tetrachloride.[21] Lazareff [129] investigated the photo-oxidation of solid dyes by oxygen at various pressures up to 120 atmospheres, and found that, as the pressure increased, n, originally unity, steadily fell. In the reactions between titanium tetrachloride and mandelic acid [124] and between uranyl sulphate and

oxalic acid [122] in aqueous solution, the same dependence of n on the concentration of the organic acid was experimentally found—a zero value at high concentrations, becoming greater as the concentration was decreased. The best known exception to this rule is perhaps afforded by hydrogen in the hydrogen–chlorine reaction, where n can approach $-0{\cdot}5$ in certain circumstances.[36b] We are here, however, dealing with a definite inhibiting action of the hydrogen, bound up with the simultaneous presence of oxygen.

(iv) *Absorbed Light and Velocity.*

The form of the function connecting these two magnitudes is intimately bound up with what has been discussed in the two preceding sections, *i.e.*, it depends on the relation of intensity to velocity, and on the reaction orders for the absorbing and non-absorbing reactants. The simplest case occurs when velocity is proportional to the first power of the intensity, and all the relevant values of n are zero. Velocity will then be proportional to the absorbed light, independent of any of the concentration terms in the system (incidental complications apart), and moreover will have the maximum value possible with the given experimental conditions (light source, disposition of reaction vessel, temperature, etc.). In any case, if the order for the absorbing substance is of the $0 \longrightarrow 1$ type and the concentration of any non-absorbing substance sufficiently high, the velocity at any instant will be proportional to the rate of absorption of light.

It does not seem necessary to give a list of reactions in which such proportionality has been found. In any case, it clearly exists in all those reactions where the Einstein Photochemical Equivalent Law holds. Where the true order of n for the absorbing substance is other than unity, this proportionality will disappear. Thus, in those cases [99] [107] where n is $0{\cdot}5$, the velocity is proportional to the square root of the rate of absorption of energy. Whilst in cases where $n = 2$ (*e.g.*, the hydrolysis of the chloroplatinic acids [95] and possibly the decomposition of hydrogen peroxide solutions [127]) an increase in the rate of absorption of energy caused by increasing the concentration of the absorbing substance will bring about a proportionately greater increase in velocity.

(v) *Temperature and Velocity.*

This relation has been determined for a large number of reactions, too many to enumerate. The values obtained still justify the truth of the statement that the temperature coefficients of photochemical reactions are, as a rule, less than those of thermal reactions. Thus, omitting reactions in solids, values of $1{\cdot}05$ or less are reported by

Berthelot [130a] for the photolysis of aqueous solutions of lævulose and of oxalic acid–ferric chloride mixtures, by Bolin and Linder [131] for the decomposition of Fehling's solution in glass, by Plotnikov for the oxidation of aqueous ethyl alcohol by ammonium dichromate [119] and for the polymerisation of vinyl chloride,[132] by Padoa and Minganti [133] for the decomposition of Eder's solution in ultra-violet light, by Bodenstein [13] for the union of chlorine and carbon monoxide and for the chlorine-sensitised reaction between oxygen and carbon monoxide, by Kuhn [103, 134] for ammonia decomposition, by Rideal and Norrish [123] for the decomposition of permanganate solutions, and by Anderson and Robinson[122] for the uranyl sulphate–oxalic acid reaction. On the other hand, temperature coefficients as high as 3 are noted (before 1914, the only reactions known with values greater than 1·5 were certain oxidations in red light investigated by Trautz,[135] and the bromination of toluene [136]), particularly in a number of reactions between oxalic and formic acids (or their salts) and oxidising agents, worked on by Dhar [23d] and by Berthoud and Bellenot.[99] These reactions have comparatively high dark reaction velocities, a fact which may well be significant. Temperature coefficients less than 1 are reported by Trautz [19] for the union of chlorine and sulphur dioxide, by Bodenstein [137] for the union of chlorine and carbon monoxide (confirming a former observation of Chapman and Gee[138]) and by Padoa[139] in the case of the hydrogen–chlorine reaction, when carried out in presence of a trace of iodine, above 20°, and in blue or violet light.

Plotnikov [64] still holds to his view that the temperature coefficients of all photochemical reactions can be divided into three groups, centring around values of 1·03, 1·20, and 1·40. But the evidence is strongly against him. In only one case (Kuhn's work on ammonia decomposition [134]) has the temperature coefficient been referred to the same amount of light absorbed at the different temperatures. This point is important if there is any appreciable change in extinction coefficient with temperature.

One relation of importance emerges from the mass of data. The temperature coefficient of a given reaction sensitive to a whole series of frequencies would appear to increase with increasing wavelength. For example, Padoa and Minganti,[133] for the decomposition of Eder's solution, found a value of 1·05 for ultra-violet light, increasing to 1·75 for green light, whilst Padoa and Butironi,[43] for the hydrogen–chlorine reaction, found 1·17 for ultra-violet light, increasing to 1·50 for green light. Similarly, for hydrogen peroxide decomposition, Tian [9] found 1·15 when using a light source rich in short ultra-violet radiation, whilst Mathews and Curtis [140a] obtained 1·5 (imagined by them to be rather too high) employing a Uviol

lamp, and Kornfeld,[127] also using low-frequency ultra-violet light, got 1·32. Griffith and McKeown [141] quote similar figures for ozone decomposition. In view of the fact that thermal temperature coefficients become less at higher temperatures, the analogy drawn by Boll [95] and by Berthelot [130, 98] between temperature in thermal reactions and frequency in photochemical reactions gains interest from the above data. One exception to the generalisation has been reported, also by Padoa,[142] who finds that, for the reaction between hydriodic acid and oxygen in aqueous solution, the temperature coefficient decreases with increasing wave-length. An important paper by Tolman [143b] on the theory of the subject will be mentioned later.

(vi) *Photosensitisers and Photocatalysts.*

By *photosensitisers* are understood those substances which, when added to a chemical system, by virtue of the light they themselves absorb without undergoing permanent change, make the system sensitive to light in a frequency region where it was previously non-sensitive, or, less strikingly, materially increase its photosensitivity in a certain part of the spectrum. The most interesting newly discovered examples of photosensitisation, in which the halogens,[13, 14, 15, 16, 17, 18, 21] mercury,[3, 4, 6] and zinc oxide [8, 34] are the photosensitisers, have already been mentioned.[144] Such photochemical reactions are clearly simpler in one respect than reactions in which the absorbing substance disappears during the insolation, and, as such, are being made the subject of much study. Some of the conclusions already drawn will be mentioned later. Reference may here be made to two suggestive papers on optical sensitisation by Winther,[8, 145] to Baur's views on the same subject,[146] and to the work of Fajans [147] on the sensitisation of solid silver bromide by ionic adsorption.

Photocatalysts are, strictly speaking, those substances, which, when added to an insolated system in which a photochemical reaction is already taking place, increase the speed of this reaction without in any way affecting the amount of light of the effective wave-length absorbed, or undergoing any permanent change. From this point of view, many so-called photocatalysts are really photosensitisers, as, for example, is the case in certain of the organic decompositions and oxidations brought about in visible light in presence of small quantities of ferric or uranyl salts. Our knowledge of the mode of action of photocatalysts themselves is scanty, although some very interesting work has been done during the years under discussion. Much of this relates to the catalytic effect of traces of water vapour, which is just as striking in photochemical

as in thermal reactions. Intensive drying will more or less completely inhibit the combination of chlorine with carbon monoxide [13, 39a, b] and with sulphur dioxide,[14, 39a, b] and the dissociation of hydrogen chloride.[39a, b] It similarly inhibits the union of hydrogen and chlorine in visible light,[39a, b, c] but not completely unless the water vapour pressure is reduced to a calculated figure of 10^{-7} mm.[39d] In ultra-violet light, even drying to this limit still permits of complete combination.[39c] According to Coehn and Tramm, drying has no effect on the photochemical union of hydrogen and oxygen,[148] or on the decomposition of hydrogen bromide or iodide.[39a, b] Baker and Carlton [5b] dispute the first of these results, finding water to be a positive catalyst. The case of the reaction $2CO + O_2 \rightleftarrows 2CO_2$ is a curious one. Coehn and Sieper [149] confirm the former observations of D. L. Chapman, Chadwick, and Ramsbottom [150] to the effect that water vapour is a *negative* catalyst for the dissociation, whilst Coehn and Tramm [151] find it to have no influence on the combination. Some of the explanations given of the above results will be considered in Section IV (iii) *e*.

The work of Griffith and his collaborators on the effect of various gaseous additions on the deozonisation of ozone by visible and long-wave ultra-violet light is of interest. In the presence of hydrogen, this decomposition is catalysed (quite apart from the simultaneous chemical interaction with the hydrogen), and the results are interpreted in terms of fruitful collisions between newly-formed, high-energy water molecules and ozone molecules.[126] In a second paper,[152] the effect of other gases is investigated and compared, and found to increase in the order CO_2, CO, Ne, A, He, H_2. The same type of collision theory fits the results best.

(vii) *Negative Photocatalysts and Inhibitors.*

The study of this subject has resulted in the discovery of new facts, but of little else. Oxygen, in addition to the many known reactions, has been found to retard the decomposition of solutions of organic ferric salts,[76] and also one of the photo-changes undergone in light by tetrabenzoylethylene.[153] On the other hand, Boll and Henri [154] showed that it had no effect on the photolyses of solutions of the chloroplatinic acids or of dilute UO_2SO_4–$H_2C_2O_4$ mixtures, facts which were used by them to refute the general *rôle* assigned by Bodenstein [155] to oxygen in photochemical reactions. M. C. C. Chapman [36a] has shown that, in the case of the hydrogen–chlorine reaction, the retarding effect of oxygen is probably bound up with the fact of the presence of hydrogen. The same view, in a special sense, is taken by Norrish,[46] whilst Göhring [48] and Cathala [51] believe chlorine dioxide formation to be the explanation. Theories

of general application are put forward by Weigert [83b] and by Winther,[145] based respectively on the oxygen molecules being acceptors for electrons or for active secondary radiation. Water retards carbon dioxide dissociation,[149] the chlorine-sensitised combination of carbon monoxide and oxygen,[13] and (when present in larger amounts than for the gas reactions) the reduction of aromatic ketones by alcohols,[118] the polymerisation of vinyl chloride,[132] and the transformation of *N*-chloroacetanilide into *p*-chloroacetanilide.[156]

Nitric oxide and sulphur dioxide are negative catalysts for the chlorination of methane [53] and the dissociation of carbon dioxide [39b] respectively, whilst examples of reaction products themselves acting as inhibitors are furnished by hydrogen bromide in the hydrogen–bromine reaction [107] and by hydrogen in ammonia decomposition.[103] (More cases have also been observed in which the product of reaction retards by the mere fact of its absorbing the active radiation—*internal light filter* action or *negative photosensitisation.*) In several cases of photo-oxidations of organic acids by metallic salts, chlorine ions have been found to exert a marked retarding effect.[105, 124, 157, 158] Retarding agents for the decomposition of chlorine water have been worked on by Milbauer [57] and by Benrath and his pupils,[58, 59] and for the decomposition of hydrogen peroxide solutions by Mathews and Curtis [140] and by Anderson and Taylor.[159, 61] What seems to be a significant contribution to the study of the mechanism of inhibitors in gaseous reactions, is the paper of Norrish [46] on the effect of ammonia on the initial stages of the hydrogen–chlorine reaction, in which much evidence is brought forward in favour of the reaction being a surface one.

(viii) *Solvent and Velocity.*

No systematic investigation on these lines has been carried out, and the data which have appeared are not very conclusive. Andrich and Le Blanc [77] find the bromination of toluene in short ultra-violet light to proceed less rapidly in pure toluene than in hexane solution, and still more slowly in ethyl acetate solution. As mentioned already, they connect these changes with the nature of the absorption curve and solvation of the bromine. Olivier [160] finds the acid chlorides of benzenesulphonic acid derivatives to be oxidised by air more easily in ether than in chloroform, whilst there was no action in carbon tetrachloride or in carbon disulphide. According to von Euler,[161] the photo-decomposition of the halogenoacetic acids is far more rapid in ether than in benzene solution. Meyer and Eckert [162] obtain more rapid oxidation of dihydroanthracene dis-

solved in acetic anhydride or in ethyl alcohol than in methyl alcohol. Stobbe and Schmitt,[163] in studying for various wave-lengths the oxidation by air of ethyl iodide dissolved in carbon tetrachloride, benzene and alcohol, found complex differences, apparently depending on internal light-filter action, or photosensitisation by liberated iodine, etc. Swensson [164] finds benzene, and still more, alcohol, to retard the bromination of xylene and toluene. In the latter case, he connects the effect with the fixation by the alcohol of hydrogen bromide, which is a positive catalyst. Lifschitz and Joffe [165] have studied the changes of certain leuco-derivatives of the triphenylmethane series in ultra-violet light, and find more rapid reaction in alcohol than in ether or benzene. According to Plotnikov,[132] the solvent has a considerable effect on the polymerisation of vinyl chloride. The best results are obtained in methyl alcohol. In carbon tetrachloride the reaction is rapid at the start, whilst in carbon disulphide, nothing happens. In benzene, the results are abnormal. Mathews and Williamson [156] show that the rate of formation of *p*-chloroacetanilide from *N*-chloroacetanilide depends on the solvent, and moreover in the order ethyl alcohol > benzene or glacial acetic acid > dilute aqueous acetic acid. Water here plays an important *rôle*. Winther [166] has directed attention to an apparent relation between rate of reaction and dielectric constant of solvent.

(ix) *Photochemical Stationary States.*

A system is said to be in a photochemical stationary state when its final composition in a light field of constant intensity and quality is different from the composition corresponding to thermodynamic equilibrium, and when, on cutting off the light, it changes, or tends to change, to the thermodynamic equilibrium state. Prior to 1914, it was thought by some (*e.g.*, by Coehn) that such stationary states were governed by the mass-action law, but this is now recognised by all not to be so. Their formation and existence result from the opposition of two reaction velocities, but at least one of these is a photochemical reaction velocity, not subject to the ordinary laws of dark chemical kinetics.

The possible types of stationary state which may occur have been discussed by Coehn and Stuckardt [78] and by Le Blanc.[14] Coehn and Sieper [149] have investigated the case of carbon monoxide–oxygen–carbon dioxide, where the presence or otherwise of water vapour has a remarkable and profound effect. Coehn and Stuckardt [78] have worked on the synthesis and decomposition of hydrogen chloride, bromide, and iodide, and on the effect of wave-length on the stationary states. Le Blanc [14] has studied the complex case of

sulphuryl chloride–sulphur dioxide–chlorine. The liberation of iodine and the existence of a photo-equilibrium in insolated systems containing uranyl salts and hydriodic acid have been demonstrated by Hatt,[105] and Rideal and Williams [25] have investigated a similar reaction where a ferric salt takes the place of a uranyl salt. A number of cases of stationary states set up under the influence of ultra-violet radiation have been reported in connexion with *cis*- and *trans*-stereoisomerides.[167, 168] In one of these—the trans-formation maleic acid $\rightleftarrows$ fumaric acid—the stationary state concentrations found by Kailan [169] agree well with the values calculated by E. Warburg [170] from his measurements of the energetics of the two component reactions. Other systems in which stationary states have been described include phenylacetaldehyde and its polymeride; [171] the very complex case of hydrogen–oxygen–water–hydrogen peroxide examined by Tian; [9] α-phenylcinnamonitrile, bromine, and the addition product; [125] leuco-compounds of the triphenylmethane group, and the corresponding colouring matters; [165] aqueous solutions of potassium nitrate in ultra-violet light.[172] In the last example, the opposing dark reaction suggested is

$$KNO_2 + O \longrightarrow KNO_3.$$

(x) *Photochemical Extinction.*

Little need be said here. No cases have been reported, and investigators clearly do not expect to find them. The reason is that, whereas the theory of electromagnetic absorption of light did not contradict the possibility of the existence of such a phenomenon, the case is otherwise with the discontinuous theory of absorption, which sharply separates off light absorption and subsequent chemical happenings. On the older theory, photochemical extinction or "chemical absorption" was looked on by some as exceedingly probable, as can be seen from a paper of Tian.[9] It may be added that Winther, in his 1909—1913 report,[2] did not dismiss the possibility in the case of endo-energetic or "work-storing" reactions.

(xi) *Photochemical Induction.*

Some new cases have been noted and are generally explained by the former theories—the gradual destruction of an inhibitor or the formation of a positive catalyst by light. In some instances, the dark production of a photo-sensitiser has been shown to be responsible for the inception of the photo-reaction. Examples of the last type of action are furnished by nitrogen pentoxide decomposition,[30] and the oxidation of hydrogen iodide by oxygen in aqueous solution,[17] where the thermal production of nitrogen peroxide or of I_3^- ions respectively is necessary before the photo-reaction can

commence. In the decomposition of hydrogen peroxide solutions in presence of potassium ferrocyanide,[173] the formation in light of a photo-catalyst is clearly responsible. Destruction of a negative catalyst (an ammonium salt) was shown to determine the induction period in the oxidation of potassium oxalate by bromine in aqueous solution,[99] and a similar state of affairs probably exists in an aqueous solution of formic acid containing added uranyl and vanadyl salts, which shows marked induction.[105] Induction periods were also noticed during the reduction of carbonyl chloride by hydrogen,[22] the chlorine-sensitised union of carbon monoxide and oxygen,[13] the photolysis of oxalic acid, whether solid or in solution,[93] the reaction between bromine and tartaric acid in aqueous solution,[174] and in the chlorination of certain aliphatic derivatives in carbon tetrachloride solution.[55] The papers of Norrish [46] and of Jones [72] are of importance from the point of view of the mechanism involved in inhibited chlorine reactions, and it is of interest that both introduce the surface of the vessel as a factor. Finally may be noted that a curious "negative induction" is reported by Kornfeld and Müller [42] in very sensitive hydrogen–chlorine mixtures.

(xii) *After-effects in Photochemical Reactions.*

These have been found to occur in the cases of the reaction between *p*-nitrosodimethylaniline and potassium ferrocyanide [175] and the decomposition of hydrogen peroxide solutions in presence of this salt,[173] in the bromination of toluene, hexane, and heptane,[176] and the reaction between aqueous bromine and tartaric acid,[174] in the decomposition of Fehling's solution in ultra-violet light [131] and the transformation of *N*-chloroacetanilide into *p*-chloroacetanilide.[156] The suspected and sometimes proved cause of such a phenomenon is usually the production of a "dark" catalyst during the photo-reaction.

After-effects of a different nature, depending on the formation during the photochemical reaction itself of an essential intermediate product, whose subsequent rate of reaction is sufficiently slow to enable its presence to be detected after the cessation of illumination, have been studied for the first time by Weigert and Kellermann [38] in connexion with the initial stages of the hydrogen–chlorine reaction, and by D. L. Chapman,[106] who has followed up some observations of Berthoud and Bellenot.[99] Their further investigation promises to be of quite special interest.

(xiii) *Analogies between Photochemical and Other Types of Chemical Change.*

Such comparisons are frequently, from a limited point of view, of considerable interest. Boll [95] and Berthelot [130, 98] have directed

attention to the analogy, from the point of view of kinetics, between the effect of temperature in thermal reactions and frequency in photochemical reactions. The Einstein Photochemical Equivalent Law [see III (iii)] has been compared with Faraday's Law of Electrolysis,[177, 80, 178] and frequency with decomposition voltage.[98] Baur has worked out in detail a whole theory of photochemical change on an electrochemical analogy, imagining the absorption of light to polarise the molecule, with subsequent "electrolysis" and formation of "anodic" and "cathodic" products.[146, 158, 34, 179] A comparison between the chemical action of the silent discharge and that of light is made by E. Warburg.[180] Berthelot [98] and Bancroft [181] have pointed out resemblances between photochemistry and fermentation reactions and contact catalysis respectively.

III. *Energetics.*

(i) *Thermodyamics and Photochemistry.*

The irruption of the quantum theory into photochemistry has profoundly modified the point of view from which the energetics of the subject is regarded. Before this event, many attempts were made (particularly by Trautz, Weigert, and Byk) to treat photochemical problems by the aid of classical thermodynamics. Such attempts had no great success, and the reason is obvious if the quantum theory be accepted. There is clearly a fundamental incongruity between, on the one hand, the generalised, non-specific methods of classical thermodynamics as applied, for example, to a case of thermal equilibrium, and, on the other, the "activated" molecule resulting from an individual elementary photochemical process, and capable, in virtue of its specific energy content, of kinetic behaviour of a type quite different from that of the surrounding "un-activated" molecules. According to Nernst and Noddack,[182] the only valid application of thermodynamics to photochemistry is the decision as to whether or not a particular dark reaction is a possible one for the primarily formed activated molecule.

(ii) *Radiation Theory of Chemical Kinetics and Photochemistry.*

Two main applications of the quantum theory to photochemical energetics can be distinguished, and others will doubtless come. The first, which has attracted much attention during the last few years, is based on the Radiation Theory of Chemical Reactivity, which is a combination of Planck's radiation theory with ideas founded on thermodynamics and statistical mechanics and previously put forward by Arrhenius and Marcelin. W. C. McC. Lewis, Trautz, and Perrin have independently developed forms of this theory, and it is perhaps Perrin [183] who has most explicitly regarded

photochemical reactions as particular cases of thermal reactions, with a consequential similarity of treatment. It has already been pointed out [Section II (i)] that a relative lack of success has in practice attended this attempt at assimilating photochemical with thermal reactions. Mention of a paper by Winther [184] may be added in this connexion. In any case, the soundness of the whole "radiation" treatment of thermal reactions, particularly in its simplest form, has been strongly challenged. Tolman [143] has put forward a modified form of the theory, based on statistical mechanics and the quantum theory, and embracing photochemical reactions, whilst Weigert [185] has discussed similar modified views in a more qualitative way.

(iii) *The Photochemical Equivalent Law.*

The other, and more important, quantitative application of the quantum theory is contained, of course, in the Einstein Law of the Photochemical Equivalent. The Reporter has recently discussed fully certain aspects of this law, and, to save space, will refer readers to this paper [178] for details, and deal with the subject here in outline only (see also [80, 182, 185]). The law itself in its simplest form, *viz.*, that photochemical decomposition of a single molecule results from the absorption of a single quantum by this molecule, was formulated prior to 1914 and a thermodynamic proof given.[1a,b,c] A deduction of the relation on different lines appeared later,[1d] and made it clear that the law only applies to the primary process of photochemical change, and, further, that this primary process is normally, not a disruption of the absorbing molecule, but an activation of the same, followed by chemical reaction of the activated molecule. The activated form as described has the properties of a higher Bohr state, and it is questionable whether the law will hold for other types of primary product, even supposing them to be formed, which also is doubtful.

Much experimental work has been carried out during the last twelve years with a view to test the predicted relation between absorbed energy and amount of photochemical change. Details have been given elsewhere,[178] and mere reference will be made to the papers of Warburg,[81, 80, 180, 186, 170] Berthoud and Bellenot,[99] Bodenstein,[13] Boll,[95] Bonhoeffer,[16] Book and Eggert,[54] Bowen,[13, 14, 187] Büchi,[116] Eggert and Borinski,[128] Eggert and Noddack,[188] Grüss,[21] Hatt,[105] Kornfeld,[127] Kuhn,[103, 134] Noddack,[20] Pusch,[176] Rideal and Norrish,[189] Rideal and Williams,[25] Rudberg,[117] Vranek,[104] Weigert and Schöller,[190] and Winther and Oxholt-Howe.[76] A convenient and rational nomenclature in which to express the results has been drawn up by Warburg.[80, 178]

Work not included in the above list is summarised in the following table, where γ signifies the *quantum efficiency*, or the number of absorbing molecules which have reacted per quantum absorbed.

Reaction.	Author.	γ.	Remarks.
Chlorophyll sensitisation of CO_2 assimilation.	O. Warburg and Negelein.[109]	In molecules of CO_2, 0·23 for 0·66 μ, 0·23 for 0·578 μ, 0·20 for 0·436 μ.	
I_3^- sensitisation of O_2+HI (aqueous solution).	Winther.[110]	In molecules of HI, 6·5—83 for 0·366 μ.	Varies regularly with rate of absorption of energy by system, increasing as this becomes less. For same rate of energy absorption, practically independent of λ between 0·280 μ and 0·436 μ.
Dissociation of NOCl.	Bowen.[86]	1·91—2·17 for 0·47 μ.	
Dissociation of Cl_2O (sensitised by Cl_2).	Bodenstein and Kistiakowski.[15]	2·0 for 0·43 μ.	Same for direct as for sensitised reaction.
H_2+Cl_2.	Marshall.[41]	Up to $2·8\times10^4$ for 0·35 μ.	Falls with decreasing pressure. Used low pressures and H_2 excess.
H_2+Cl_2.	Kornfeld and Müller.[42]	$2·54\times10^4$ for 0·436 μ.	Ordinary gaseous pressures.
$UO_2SO_4+H_2C_2O_4$.	Anderson and Robinson.[122]	In molecules of $H_2C_2O_4$, 0·05 for 0·20—0·28 μ; 0·027 for 0·365 μ.	For 0·1*N*-$H_2C_2O_4$+0·01*M*-UO_2SO_4. Became less if $[UO_2SO_4]$ were decreased.
$H_2C_2O_4$ decomposition.	,,	0·0007 for 0·20—0·30 μ.	
o-$C_6H_4(NO_2)\cdot CHO \longrightarrow$ *o*-$C_6H_4(NO)\cdot CO_2H$	Weigert and Brodmann.[191]	0·40—0·61 for 0·366 μ; 0·39—0·52 for 0·405 μ; 0·34—0·65 for 0·436 μ.	Independent of concentration.

The actual values of quantum efficiency found vary enormously—in the period under review between 2·5—2·8 $\times$ 10^4 for the hydrogen–chlorine reaction [41, 42] and 0·0007 for decomposition of aqueous solutions of oxalic acid.[122] On the strict original interpretation of the law, the value unity should be got in every case, independent of wave-length and intensity of light, concentration, the presence of other substances, and temperature. This is far from being the case. The nature of the discrepancies found has been dealt with elsewhere.[178] Here it will only be stated that γ usually increases with frequency, often with concentration and with temperature (although only one case of the latter kind has actually been measured),[134] and is frequently dependent on the presence of other

substances (positive and negative catalysts). In Kuhn's experiments on ammonia decomposition,[103] he found γ to decrease with increasing homogeneity of light. The effect of intensity is not very clear. Winther [192] has recently discussed cases in which the greater the rate of absorption of radiation (which brings in intensity and concentration) the smaller is the quantum efficiency. In the hydriodic acid–oxygen reaction, sensitised by I_3^- ions, he considers that only those I_3^- ions which absorb a single quantum are capable of causing the formation of iodine—those which take up more than one quantum are inactive. On the other hand, the experimental results and the theory put forward by Pringsheim,[113, 114] in connexion with the destruction of fluorescent dyes by light, indicate that the quantum efficiency should increase with the radiation density and the concentration.

It is not surprising that certain authors, more particularly Plotnikov,[193] should have protested against the application of the term "law" to the Einstein photo-equivalent relation. Its validity within well-defined limits, and the usefulness of the conception, cannot, however, be denied, and some of Plotnikov's counter-proposals are distinctly retrograde. A juster appreciation is contained in a paper by Nernst and Noddack.[182] The first step in a photochemical reaction is undoubtedly the absorption of a single quantum by a single molecule. This may or may not result in the "activation" of the molecule—the "activated" molecule, if formed, may or may not undergo or take part in a secondary stoicheiometrical dark reaction. These two main causes of deviation from the Einstein relation will be considered in the next section of this Report.

IV. *Mechanism of Photochemical Change.*

(i) *Preliminary.*

A consideration of this subject naturally divides itself into two parts, one dealing with the mechanism of the primary photochemical effect, the second with that of secondary thermal reactions. In respect of both of these sub-divisions, we have reached a very interesting stage of development, and it seems likely that, in the next few years, many of the questions at present in the foreground will be substantially, if not completely, answered. The advance here forecasted will primarily be due to an increased knowledge of the mechanism of absorption of light by molecules and of its consequences, and to a more certain interpretation of the significance of spectral data. Too many of the views put forward during the last twelve years have taken little account of our existing store of

knowledge on these subjects, and, as the latter increases, it is safe to prophesy that other views held to-day by many photochemists will have to be jettisoned.

(ii) *The Primary Process.*

(a) *Dissociation.*—Probably influenced by the fact that, in the original proof of the Einstein law,[1a] the primary process taken as an example was a monomolecular dissociation, it was assumed early that, provided that the absorbed quantum was greater than the energy needed to dissociate a single molecule (q_0), such dissociation was bound to occur as an immediate result of absorption. Thus, Warburg suggested the following as primary reactions—for ozone formation, $O_2 \longrightarrow 2O$; [186a] for gaseous hydrogen bromide [186b] and iodide [186c] decomposition, the monomolecular dissociation of the halogen hydride. Nernst [47, 177, 194] proposed the reaction $Cl_2 \longrightarrow 2Cl$ as the primary process in the photosynthesis of hydrochloric acid, and this was concurred in by Göhring,[48] Berthoud,[50] and Cathala.[51] Bowen [85] treated the whole of the photochemistry of the halogen hydrides from the same point of view. Primary monomolecular dissociations were also proposed for the photolyses of ammonia [103] (into $N + H_2 + H$), nitrosyl chloride,[86] certain classes of aliphatic compounds,[87] and solutions of uranyl oxalate [116] and potassium permanganate,[189] as also for the reactions of bromine or iodine with potassium oxalate [99] and of hydrogen with sulphur vapour ($S_2 \longrightarrow 2S$).[31]

Stern and Volmer,[195] in a very important paper, were the first to point out that certain fluorescence phenomena (*e.g.*, of iodine vapour) showed that a molecule could absorb and re-emit a quantum several times greater than corresponded to the energy of dissociation without being split up. Combining this fact with Bohr's views on light absorption, they asserted that the primary product of light action would invariably be an activated molecule with an atom in a higher quantum state (Bohr state). Collision with another molecule (not necessarily of the same nature, and, still less, activated) would always be necessary for chemical change. Such chemical change might well be dissociation of the absorbing substance—but as the result of a collision or secondary reaction. Warburg, who had previously [186b] applied Stern's conception of a bimolecular reaction to cases where $h\nu < q_0$ (*e.g.*, to ammonia dissociation), agreed that activation in the Bohr sense is probably the immediate result of absorption, but would not exclude the possibility of an immediately subsequent monomolecular dissociation.[180] However, the views of Stern and Volmer have recently gained general acceptance. For example, the first stages

of the hydrogen–chlorine reaction have been formulated by Coehn and Jung [39c] as (*a*) $Cl_2 + h\nu \longrightarrow Cl_2'$, (*b*) $Cl_2' + Cl_2 \longrightarrow Cl_2 + 2Cl$. This change in opinion is largely due to the work of Born and Franck,[196] who have analysed the possible conditions under which a molecule can decompose as a direct result of absorbing radiation, and come to the conclusion that a subsequent collision with another molecule of some sort or another is necessary. In view, however, of the hydrogen–chlorine mechanism just mentioned, it is interesting to note that Franck,[197] in a very recent paper, states that certain types of homopolar molecules, including the halogens, *can* be *directly* dissociated, into a normal and an excited atom, by absorption of light of wave-length shorter than the long wave-length limit of the continuous absorption band. In the case of chlorine, this corresponds with the experimental result, already mentioned, found by W. Taylor.[44]

(b) *Activation.*—In contrast with the clear idea of the "activation" of an atom afforded by the conception of the higher Bohr state, with an actual loss of an electron as a limiting case, our views on the nature of an "activated" molecule are relatively obscure. According to Volmer,[198] who found the electrical conductivity of various photosensitive substances to increase on insolation, the activation consists in a loosening or partial separation of valency electrons. The same view was put forward by Bodenstein,[47] as a modification of his former theory [155] of complete electron separation as the primary process. It is also adopted by Lazareff,[129] and has been developed in recent years in a number of papers by Weigert,[190, 199, 83, 73, 185] who ascribes photochemical reactions in solid systems to an actual passage of an electron from one particle to another. Electron loss mechanisms are also postulated for specific reacting solid systems by Fajans,[147] and by Moore and W. A. Noyes, jun.[5] Baur's [146, 158, 34, 179] view that an activated molecule is polarised or partially ionised has already been dealt with. The limiting case of this conception—ionisation into positive and negative ions—has not been proposed. Finally, Warburg [170] suggests that an activated molecule is one in which the constituents (uncharged) have been widely separated as the result of the absorption of a light quantum. If the separation becomes complete, we have the case of dissociation already dealt with.

Recent physical work [196, 197, 90] enables us, in some measure, to decide between these conceptions. The essential result of the absorption of a quantum of visible or ultra-violet light is to raise a valency electron to a higher quantum state. The internal configuration of the molecule is thereby changed, and there is, as a secondary result, an increase in the rotation and oscillation quan-

tum numbers, *coupled with, and determined by*, the increase in electronic energy. The change in rotational energy is small, and can be neglected. If the absorbing molecule is heteropolar, *e.g.*, hydrogen bromide, the increase in energy of oscillation is also proportionately small, and there is no chance of a monomolecular dissociation (which would be into ions, and not into atoms) taking place. If the absorbing molecule is homopolar, the state of affairs is somewhat different. With a certain type of linking (by van der Waals's forces, as Franck puts it), it is possible for the molecule to take up large amounts of oscillation energy, so much so, that dissociation into an excited and a normal atom eventually results. The halogens, as has been seen above, probably come under this category. With another type of homopolar molecule, linking by shared electrons, of which hydrogen and oxygen form examples, although oscillation energy can be very much increased by light absorption, there is no chance of a monomolecular dissociation into atoms.

It thus appears that, in general, the "electron-loosening" mechanism of Stark [200] (compare Luther's very similar views),[79b] supported, as we have seen, during the last twelve years by Volmer and others, describes the state of a photo-activated molecule better than the other conceptions put forward by photochemists. Baur's polarisation idea corresponds, qualitatively only, to what happens (in addition) in heteropolar molecules, and Warburg's conception of the partial separation of neutral constituents can be applied (in addition) to homopolar molecules. In any case, these activated molecules represent unstable systems, with a strong tendency to part with their energy of activation.

Activation does not, of course, necessarily follow absorption. The increase in energy brought about by the absorption of the quantum may be too small to activate the molecule for the particular reaction. This will be so if the absorbing molecule is originally in too low a quantum state. This aspect of the subject has been treated by Tolman,[143b] who has shown the connexion between the temperature coefficient of the reaction and the proportion of molecules which will be in a position to react as the result of quantum absorption. Weigert [185] also has laid emphasis on the importance of the initial energy state of the absorbing particle. If the reaction is bimolecular, the total heat of activation can, in principle, be contributed to by the two reacting molecules. Bodenstein [201] considers the bromination of toluene from this point of view. H. S. Taylor and Marshall [4] show that, in the mercury-sensitised reduction of carbon monoxide by hydrogen, the carbon monoxide is probably not activated.

(c) *Life of Activated Molecules.*—This is obviously an important question, as collision between an activated molecule and some other one is normally necessary before reaction of any kind can take place. The nature of an activated molecule being as explained, it follows that its life must be of the same order as that of a higher Bohr state, *i.e.*, 10^{-7}—10^{-8} second (for a list of the determinations, see [40]). Noddack [20] and Grüss [21] calculated for particular cases values of the order of 10^{-9}—10^{-7} second. The negative results of Le Blanc and Volmer and others,[65, 66, 67] on the insolation of chlorine before allowing it to come into contact with hydrogen, are in qualitative agreement, and, as Warburg [180] has pointed out, are evidence against the assumption that chlorine atoms are the primary product of light action in this case. There is, however, one class of reactions the kinetics of which appears to indicate the existence of activated molecules of comparatively long life, *i.e.*, reactions photo-sensitised by halogens.[202] Franck, Nernst and others have expressed the opinion [128] that halogens must be capable, in some way or other, of stabilising a quantum taken up in a higher Bohr state. Possibly the explanation may be a metastable halogen molecule, of the type postulated by Franck and Grotrian [203] to explain the long-lived fluorescence which can be excited in mercury vapour under certain conditions. There may also be mentioned here a paper by Tolman,[204] which contains calculated examples of durations of higher quantum states amounting to as much as one second.

(iii) *Fate of Activated Molecules.*

(a) *Deactivation by Radiation.*—We have seen that molecules of a certain particular kind can (probably) break up spontaneously as the result of the absorption of a sufficiently large quantum. In other cases, however, if they do not, during their life period, encounter another molecule, collision with which will bring about chemical reaction, they will lose energy, and revert to the unactivated condition. Cases in which this lost energy appears as radiation have been much studied by physicists (*e.g.*, resonance radiation and fluorescence in rarefied gases) and similar conceptions have been introduced to explain de-activation in photo-sensitive systems. The more energy lost in this way, the smaller, of course, will be the photochemical utilisation of the originally absorbed energy. Trümpler [205] found that oxalic acid, which quenches the fluorescence of uranyl salts far more strongly than does formic acid, undergoes photolysis in a uranyl salt mixture much more easily than does the latter. Pringsheim [113, 114] thinks that the majority of activated molecules tend to lose their energy by fluorescence, and that, for chemical action to result, the absorbed quantum must

be comparatively large, or there must be a favourable probability factor, involving a high light intensity or close proximity of two activated molecules.

Weigert,[73] in order to explain the difficulty with regard to the long life of the activated molecule in the halogen-sensitised reactions referred to above, suggests that chlorine molecules are capable of isochromatic fluorescence or resonance radiation, and that absorbed light is constantly being re-emitted and reabsorbed by other molecules until finally transformed into heat (translational energy) or chemical energy. Such resonance radiation is not observed on account of the weak absorption, and therefore weak fluorescence, of chlorine. (The "van der Waals" type of linking assumed by Franck [197] for the chlorine molecule would perhaps render such resonance radiation possible.) Weigert explains in this way the absence of the Budde effect in dry chlorine, and Ludlam [206] puts forward an identical view of the absence of the same phenomenon in dry bromine.

Winther [184, 8, 145, 207, 110] supposes the activated molecule of a photosensitiser, such as chlorine, zinc oxide, or the I_3^- ion, to lose its energy in the form of short ultra-violet radiation (*i.e.*, the molecule of the sensitiser transforms the absorbed radiation up to a higher frequency), and that it is the absorption of this radiation which brings about the sensitised reaction. He accounts for the frequent retarding action of oxygen by its absorption of this radiation, and suggests that induced (dark) reactions are caused by similar absorption of short ultra-violet chemiluminescent radiation resulting from the primary reaction.

(b) *Deactivation by Collision.*—If an activated molecule, during its life-period, strikes another molecule, a number of things may happen. Of these, the most frequent is the degradation of its energy of activation into heat (energy of translation). Physics furnishes a number of well-known examples. Thus, the resonance fluorescence of iodine or of mercury becomes weaker if the pressure of the vapour itself is increased, or if foreign gases are admixed; this is ascribed to collisions between inactive molecules and activated molecules before the latter have had time to radiate, the energy of activation being transformed by collision into kinetic energy of translation.[208] The fact that absorption lines in gases become broader at high pressures and are very generally broad in solution is regarded as evidence that the absorbing molecules are being "damped" by collision with neighbouring particles.[79] (The quantum theory substitutes for this impact damping an effect due to the fields of neighbouring atoms on the configuration and energy of the excited electron orbit in the activated molecule.[82]) Warburg [81]

ascribes to this damping the low quantum efficiencies frequently obtained in reactions in solution. The degree of activation conferred on the absorbing molecule by the absorbed quantum would be sufficient, if it could be utilised, to bring about the chemical change —but, before it can be utilised, it is reduced below the critical level by the interaction of solvent molecules. Weigert,[209] in a number of papers, has insisted on the importance, from this point of view, of taking into account the orientation and the whole environment of an absorbing molecule in a photochemical system—the absorbed quantum is very frequently only partly utilisable.

There are conditions in which such collisions between activated molecules and others do not appear to cause energy degradation, or, if they do, it is negligible in amount—the halogen-sensitised reactions already referred to. Thus, in the bromine-sensitised transformation of maleic ester to fumaric ester in carbon tetrachloride solution,[128] there must be several thousand inactive encounters between activated Br_2' molecules and carbon tetrachloride molecules before an effective one takes place. Or, alternatively, a single collision only causes a very slight energy loss. According to Stern and Volmer,[195] the greater the electron affinity of the unactivated molecule, the greater will be the energy dissipation on impact. As has been seen, it appears necessary, in the case of the halogens, to assume a peculiarly stable type of activated molecule.

(c) *Collisions with Acceptors.*—Before, however, an activated molecule radiates or loses sufficient of its energy by interaction with neighbouring particles, it may collide with an "acceptor," *i.e.*, a molecule which, in circumstances, may be capable either of reacting with the activated molecule, or of itself alone undergoing chemical change as a result of the encounter, or, by giving an opportunity for the quantised energy content of the activated molecule to adjust itself to new molecular configurations, of permitting the latter to undergo chemical change. By no means all such encounters seem to be effective in causing chemical reaction. Thus, unproductive collisions between activated and normal ammonia molecules, accompanied by energy dissipation, may account for the low quantum efficiency observed in ammonia decomposition.[186b] The same type of phenomenon, complicated by the presence of other gases, appears in the deozonisation of ozone.[126, 152, 137, 141] There is then, from this point of view, no sharp distinction between acceptors and non-acceptors.

But there can also be collisions which, whilst ineffective from the chemical point of view, and causing the deactivation, complete or partial, of the original activated molecule, do not result in this energy of activation being completely degraded; it is simply passed

on, perhaps with loss, from the one molecule to the other, the latter becoming activated. (If the two molecules are identical in chemical nature, the result is the same as an elastic collision, or one nearly so.) From the point of view of the quantum theory, the result of such an impact is simply an extreme case of the degradation of energy by collision considered in the last section.

Our knowledge of this type of collision we essentially owe to Franck. In a series of papers appearing from about 1913 onwards, he studied the interactions between moving electrons and gas atoms, and was able to show that, on collision, the kinetic energy of the electron was changed, in accordance with the quantum theory, into energy of activation of the gaseous atom (*First Type Rayless Collision*) [210] If the kinetic energy of the electron were less than the amount corresponding to the one quantum necessary, the collisions were perfectly elastic. The next step was taken by Klein and Rosseland,[211] who showed the necessity, in such circumstances, of *Second Type Rayless Collisions*, in which an atom in a high Bohr state, by encounter with an electron, completely loses its energy of activation, which is turned into energy of translation of the electron. Franck [212] extended these views so as to embrace collisions with transfer of quantised energy between activated and unactivated atoms or molecules of the same or of different kinds, and applied the conception to the transfer of energy in photochemical reactions, particularly photosensitised reactions. Thus, the photosynthesis of water by visible light in presence of chlorine [56] will proceed by primary activation of the chlorine, collision between activated Cl_2' molecules and oxygen molecules, resulting in deactivation of the former and activation of the latter, and, finally, interaction between the acceptor, hydrogen, and the activated O_2' molecules. It has also been suggested that such secondarily activated O_2' molecules may play a part in deozonisation,[202] and in the reaction between oxygen and trichlorobromomethane,[21] both sensitised by chlorine. In the former of these reactions, there must either be such rayless transfer of energy between activated and normal chlorine molecules, or else elastic collisions.

The beautiful work of Kautsky and his colleagues [213] forms an indirect confirmation of the above views, in that they have shown that chemiluminescence and the induced chemiluminescence which they discovered are the exact reversed counterparts of photochemical and sensitised photochemical reactions.

When chemical reactions result, there are several cases to distinguish. The activated molecule may undergo isomeric change, as in the transformation of maleic into fumaric acid.[170] Or it may dissociate. Thus, processes such as $Cl_2' + Cl_2 \longrightarrow 2Cl + Cl_2$,[39c] $HI' +$

$HI \longrightarrow H + I + HI$,[137] $NOCl' + NOCl \longrightarrow NO + Cl + NOCl$, $S_2' + S_2 \longrightarrow 2S + S_2$, etc., may be supposed to follow the appropriate activation processes. There is no necessity for the second molecule to be of the same nature as the first, its function being merely to allow of adjustment, in accordance with quantum mechanics,[196, 90] of the energy changes involved in the activation and subsequent chemical reaction. Thus, in the hydrogen chloride and hydrogen sulphide syntheses, the Cl_2' and S_2' molecules could equally well be dissociated by collision with hydrogen molecules.

On the other hand, it may be the activated molecule which will dissociate the normal, or in some other way change it chemically. For the four equations as written above, these two possibilities are, of course, indistinguishable as far as chemical result is concerned. In other cases, particularly in photosensitised reactions, it is quite clear that it is the normal molecule which is decomposed. Thus, we would have $Cl_2' + SO_2Cl_2 \longrightarrow Cl_2 + SO_2 + Cl_2$.

In the photosyntheses of hydrogen sulphide and hydrogen chloride by short wave-length ultra-violet light, and, therefore, with highly activated S_2' and Cl_2' molecules as primary products, the reactions $S_2' + H_2 \longrightarrow S_2 + 2H$ and $Cl_2' + H_2 \longrightarrow Cl_2 + 2H$ [39c] are conceivable. One of the best known and simplest examples of this is the dissociation of hydrogen in short wave-length ultra-violet light as sensitised by mercury vapour,[3] where we have

$$Hg + h\nu \longrightarrow Hg'.$$
$$Hg' + H_2 \longrightarrow Hg + 2H.$$

In some sensitised reactions, the high quantum efficiency obtainable shows that the activated molecule of the sensitiser is only *slightly*, and not completely, deactivated as the result of a single impact with the acceptor—the quantum is, as it were, distributed over a large number of molecules of the acceptor.[128]

Finally, we have the case where the two molecules react together on collision (Stark's *thermophotochemical reaction* [200b]). This mechanism has been proposed in many cases—*e.g.*, $NH_3' + NH_3 \longrightarrow N_2 + 3H_2$;[186b] $HBr' + HBr \longrightarrow H_2 + Br_2$;[195] $O_3' + O_3 \longrightarrow 3O_2$;[126] $Cl_2O' + Cl_2O \longrightarrow 2Cl_2 + O_2$.[15] Collisions between activated and normal molecules of the chloroplatinic acids [95] and of potassium nitrate,[81] between Cl_2' and trichlorobromomethane [182] and between Cl_2' and H_2 molecules [47, 49] are regarded as the stage following light absorption in the respective reactions concerned.

(d) *Reaction Chains.*—The summary of current views on the mechanism of photochemical change so far given does not account for cases in which γ is much greater than unity. Such reactions are, without exception, exothermic. The combination of hydrogen

and chlorine and the decomposition of hydrogen peroxide solutions are extreme cases. The products at the instant of their formation contain, not only the energy of activation originally absorbed, but also the liberated energy of reaction, and the suggestion that this energy store might in some way bring about further decomposition was an obvious one, and was made a good many years ago. Several views have been taken as to how this is brought about. Baly [37, 214] thinks that the energy excess is radiated by the product in the form of infra-red quanta of frequencies which coincide with absorbing frequencies of the original photosensitive molecules. More of the latter are thus activated. Anderson and H. S. Taylor [159] speak of the originally absorbed quanta being emitted by hydrogen peroxide molecules during decomposition, and being reabsorbed by other molecules. Kornfeld [215] has shown that no radiation is liberated during the combination of carbon monoxide and chlorine (a reaction in which γ is high) which will pass through quartz and, after its passage, bring about the combination of carbon monoxide and oxygen, although this reaction is sensitised by chlorine in a mixture in which some carbonyl chloride has already been formed. This experiment is interesting in connexion with Winther's suggestions [Section IV (iii) a].

The generally favoured explanation of the high quantum yield, however, assumes the formation of *reaction chains*, a conception first introduced by Bodenstein [155] to account for the big quantum yields in the hydrogen–chlorine reaction. These reaction chains usually fall into one or other of two classes. In the one, the primary process has, as one of its products, a free atom or group. This enters into reaction with a molecule of one of the substances originally present, forming another group or atom as a reaction product, which acts similarly, and so on, the chain of reactions being brought to an end by the gradual combination of the free atoms or groups with one another. In the other type of chain, an energy-rich activated molecule of one of the products is supposed to activate a molecule of one of the reactants by collision, this activated molecule then forming another activated molecule of resultant, and so on. There is thus a succession of rayless transfers of energy (*Franck transfers*). The chain in this case will come to an end by reason of a gradual dissipation of energy during collisions, either during the legitimate impact with the molecule of reactant, or during impact with other, non-reactive, molecules.

The best known example of the " atomic " chain is that suggested by Nernst [47] to account for the hydrogen–chlorine reaction. It is

$$\begin{aligned} Cl_2 + h\nu &\longrightarrow 2Cl. \\ Cl + H_2 &\longrightarrow HCl + H. \\ H + Cl_2 &\longrightarrow HCl + Cl, \textit{ etc.}, \end{aligned}$$

finishing by $2Cl \longrightarrow Cl_2$; $2H \longrightarrow H_2$; $H + Cl \longrightarrow HCl$. The chlorination of methane could be described similarly, with substitution of CH_3, CH_2Cl, etc., groups for H atoms. Berthoud and Bellenot [99] propose a chain of the nature

$$I + C_2O_4^{--} \longrightarrow I^- + C_2O_4^-$$
$$C_2O_4^- + I_2 \longrightarrow 2CO_2 + I^- + I, \textit{ etc.},$$

for the iodine–potassium oxalate reaction. Recently, H. S. Taylor[216] has suggested the following mechanism for the reduction of ethylene by hydrogen in presence of mercury, a reaction discovered by him in conjunction with Marshall:[4]

$$Hg' + H_2 \longrightarrow 2H \text{ (Cario and Franck reaction [3])}$$
$$H + C_2H_4 \longrightarrow C_2H_5$$
$$C_2H_5 + H_2 \longrightarrow C_2H_6 + H, \textit{ etc.}$$

In such chains, each of the steps subsequent to the primary reaction must be a spontaneous change, and exothermic. In this connexion, however, it must be remembered that the products of reaction will be in possession of a portion of the heat of reaction of the last link in the chain in which they have taken part—partly possibly as quantised energy of activation, partly doubtless as energy of translation. Further, the molecules that enter into each step will differ from one another in energy level. Consequently, a thermochemical calculation is not in a position to declare definitely that a certain step is impossible because it is (thermodynamically) endothermic. An example is furnished by the reaction $Br + H_2 \longrightarrow H + HBr$, which is certainly endothermic in this sense, a fact which was adduced as a reason why a H_2–Br_2 mixture is practically inert photochemically at the ordinary temperature.[177] Bodenstein and Lütkemeyer [107] have, however, shown, almost beyond doubt, that the reaction is an essential stage in the photosynthesis of hydrogen bromide which can be effected at higher temperatures.

Examples of the "rayless transfer" type of chain are furnished by the similar mechanisms suggested by Bodenstein [47] and by D. L. and M. C. C. Chapman [49] for the hydrogen–chlorine reaction, involving activation of chlorine molecules by HCl′ and H_2Cl_2' molecules respectively, and by Kornfeld [127] for hydrogen peroxide decomposition (complex steps involving formation and disappearance of activated $H^{+\prime}$ ions and O′ atoms).

The most direct evidence bearing on the actuality of reaction chains of one sort or another is contained in the work of Weigert and Kellermann,[38] who demonstrated the fact that hydrogen and chlorine continue combining together for a short period after the light is cut off. Recently, "rayless transfer" reaction chains have been introduced into the kinetics of thermal reactions [217] as a

possible explanation of a well-known difficulty concerning rates of reaction and activation. This is not the only recent instance which could be given of the close relations now existing between photochemical and dark kinetics.[107, 137, 141, 218]

(e) *Effect of Water Vapour.*—Mention must finally be made of the bearing of recent work on the part played by water in the union of hydrogen and chlorine and on the mechanism of the chain reaction to be adopted. Stern and Volmer,[195] taking the view that collision is necessary before an activated molecule can break up, suggested that the first stage in the reaction might be

$$Cl_2' + H_2O \longrightarrow HCl + OH + Cl$$

followed by $Cl + H_2 \longrightarrow H + HCl$, *etc.*, as in the Nernst chain. The velocity of reaction would be independent within wide limits of $[H_2O]$, as was found by Bodenstein and Dux.[219] Water was thus postulated as an essential constituent in the reaction, and there was definite, though not undisputed, evidence to show that this was the case. Coehn and Tramm [39a] confirmed the necessity for water when using visible light, and Coehn and Jung,[39c] assuming the impossibility of the (probably endothermic) reaction $Cl + H_2 \longrightarrow HCl + H$, which was implicit in Stern's mechanism, suggested the following

$$\left.\begin{aligned} Cl_2' + Cl_2 &\longrightarrow Cl_2 + 2Cl. \\ Cl + H_2O &\longrightarrow HCl + OH \\ OH + H_2 &\longrightarrow H_2O + H \\ H + Cl_2 &\longrightarrow HCl + Cl \end{aligned}\right\} \textit{etc.}$$

Weigert [73] (and later Bowen [85]) criticised this mechanism as involving water in the chain, in which circumstances $[H_2O]$ would certainly be of importance. Weigert put forward the view that an "adsorption complex" of H_2–Cl_2–H_2O is necessary for the initiation of the primary process, before the chain sets in (earlier workers had imagined such a complex) and that the presence of the water enables a smaller quantum to start the reaction than would otherwise be the case. Bowen, assuming the Nernst chain, suggested that the water acted by virtue of a surface action on the walls of the vessel, preventing the union of hydrogen atoms to molecular hydrogen, a reaction which would end the chain.

Coehn's mechanism was criticised by Cathala,[51] who pointed out that the relative numbers of impacts which would take place between chlorine atoms and water molecules on the one hand, and between two chlorine atoms on the other, in experiments quoted by Coehn and Jung,[39d] in no way corresponded with the numbers necessitated by the high quantum efficiency obtained. He suggested that the function of the water molecule, as an electric dipole with a large

stray force field, was to induce greater chemical reactivity in those molecules within its sphere of influence. Norrish [46, 220] reinforced Cathala's criticism of Coehn's mechanism, and in addition, pointed out a fallacy in the former's own argument. Like Bowen, he suggested that the effect of the water was exerted on the surface of the reaction vessel, and supported his argument by a consideration of the details of the experiments of Coehn and Jung. His view is that a water–chlorine complex, such as $\begin{matrix}H\\H\end{matrix}\!>\!O\!<\!\begin{matrix}Cl\\Cl'\end{matrix}$, is formed on the surface of the vessel, but is so structurally weakened by adsorption that light can bring about its decomposition into water molecules and chlorine atoms, the Nernst chain then following.

Chapman [106] accepts the evidence of the necessity of the presence of water, rejects Bowen's suggestion as to the part played by the latter, and proposes a chain mechanism of a new (addition product) type which may be represented as follows:

$$Cl_2' + H_2O \longrightarrow \begin{matrix}Cl\\Cl\end{matrix}\!>\!O\!<\!\begin{matrix}H\\H\end{matrix}$$

$$\begin{matrix}Cl\\Cl\end{matrix}\!>\!O\!<\!\begin{matrix}H\\H\end{matrix} + H_2 \longrightarrow \begin{matrix}H\\Cl\end{matrix}\!>\!O\!<\!\begin{matrix}H\\H\end{matrix} + HCl$$

$$\begin{matrix}H\\Cl\end{matrix}\!>\!O\!<\!\begin{matrix}H\\H\end{matrix} + Cl_2 \longrightarrow \begin{matrix}Cl\\Cl\end{matrix}\!>\!O\!<\!\begin{matrix}H\\H\end{matrix} + HCl \textit{ etc., etc.}$$

Here the subject, which is very much under discussion, can be left, and the Report concluded.

A. J. Allmand.

References

[1a] *Ann. Physik*, 1912, [iv], **37**, 832. [1b] *Ibid.*, 1912, [iv], **38**, 881. [1c] *J. Physique*, 1913, **3**, 277. [1d] *Verh. deut. physikal. Ges.*, 1916, **18**, 318. [2] *Z. wiss. Photochem.*, 1914, **14**, 19; *A.*, 1915, ii, 199. [3] *Z. Physik*, 1922, **11**, 161; *A.*, 1922, ii, 809. [4] H. S. Taylor and A. L. Marshall, *J. Physical Chem.*, 1925, **29**, 1140; *A.*, ii, 1078. For similar, less striking work, see R. G. Dickinson, *Proc. Nat. Acad. Sci.*, 1924, **10**, 409; *A.*, 1924, ii, 841. [5a] *J. Amer. Chem. Soc.*, 1924, **46**, 1367; *A.*, 1924, ii, 748. [5b] See also H. B. Baker and (Miss) M. Carlton, *J.*, 1925, **127**, 1990. [6] *J. Amer. Chem. Soc.*, 1925, **47**, 1003; *A.*, ii, 573. [7] *Verh. deut. physikal. Ges.*, 1915, **17**, 194; *A.*, 1916, ii, 526. [8] *Z. wiss. Photochem.*, 1922, **21**, 168. [9] A. Tian, *Ann. Physique*, 1916, [ix], **5**, 248. See ref. 97.

[10] *J.*, 1923, **123**, 2328. [11] *J.*, 1925, **127**, 510. [12] *Z. anorg. Chem.*, 1925, **147**, 233; *A.*, ii, 1077. [13] M. Bodenstein, *Rec. trav. chim.*, 1922, **41**, 585. [14] M. Le Blanc, *Z. Elektrochem.*, 1919, **25**, 229; *A.*, 1919, ii, 442. [15] M. Bodenstein and G. Kistiakowski, *Z. physikal. Chem.*, 1925, **116**, 371; *A.*, ii, 883. [16] *Z. Physik*, 1923, **13**, 94. [17] *Danske Vid. Selsk. Math. Phys. Medd.*, 1920, **2**, No. 2; *A.*, 1920, ii, 427. [18] *Z. wiss. Photochem.*, 1919, **18**, 227. [19] *Z. Elektrochem.*, 1915, **21**, 329; *A.*, 1915, ii, 623.

[20] *Ibid.*, 1921, **27**, 359; *A.*, 1921, ii, 568. [21] *Ibid.*, 1923, **29**, 144; *A.*, 1923, ii, 278. [22] *Thesis* (Karlsruhe), 1915. Also (less fully) G. Bredig and

A. von Goldberger, *Z. physikal. Chem.*, 1924, **110**, 521; *A.*, 1925, ii, 142, [23a] *Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1097; *A.*, 1916, ii, 236, [23b] *Ibid.*, 1920, **23**, 308; *A.*, 1921, ii, 37. [23c] *J.*, 1917, **111**, 707. [23d] *J.*, 1923, **123**, 1856. [23e] *Z. anorg. Chem.*, 1924, **134**, 172 (with R. C. Banerji); *A.*, 1924, ii, 466. [24] N. Sasaki, *Mem. Col. Sci. Kyōtō, Imp. Univ.*, 1922, **5**, 315; *A.*, 1922, ii, 772. [25] E. K. Rideal and E. G. Williams, *J.*, 1925, **127**, 258. [26] *Biochem. Z.*, 1914, **60**, 480; *A.*, 1914, ii, 321. [27] W. H. Ross, *J. Amer. Chem. Soc.*, 1906, **28**, 786; *A.*, 1906, ii, 512. [28] *J. Physical Chem.*, 1914, **18**, 641; *A.*, 1914, ii, 830. [29] *Z. Elektrochem.*, 1925, **31**, 255; *A.*, ii, 691.

[30] F. Daniels and E. H. Johnston, *J. Amer. Chem. Soc.*, 1921, **43**, 72; *A.*, 1921, ii, 249. [31] *J.*, 1924, **125**, 2070. [32] *Z. wiss. Photochem.*, 1915, **14**, 217; *A.*, 1915, ii, 504. [33] *Helv. Chim. Acta*, 1925, **8**, 403; *A.*, ii, 884. [34] *Ibid.*, 1924, **7**, 910; *A.*, 1924, ii, 857. [35] *J.*, 1919, **115**, 1264. [36a] *J.*, 1923, **123**, 3062. [36b] *J.*, 1924, **125**, 1521. [37] *J.*, 1921, **119**, 653. [38a] *Z. Elektrochem.*, 1922, **28**, 456; *A.*, 1923, ii, 3. [38b] *Z. physikal. Chem.*, 1923, **107**, 1; *A.*, 1924, ii, 8. [39a] A. Coehn and H. Tramm, *Ber.*, 1923, **56**, [*B*], 458; *A.*, 1923. ii, 205. [39b] H. Tramm, *Z. physikal. Chem.*, 1923, **105**, 356; *A.*, 1923, ii, 716. [39c] A. Coehn and G. Jung, *Ber.*, 1923, **56**, [*B*], 696; *A.*, 1923, ii, 206. [39d] A. Coehn and G. Jung, *Z. physikal. Chem.*, 1924, **110**, 705; *A.*, 1925, ii, 142.

[40] *J. Physical Chem.*, 1925, **29**, 842; *A.*, ii, 883. [41] *Ibid.*, p. 1453. [42] *Z. physikal. Chem.*, 1925, **117**, 242; *A.*, ii, 984. [43] *Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 215; *A.*, 1916, ii, 592. [44] *Phil. Mag.*, 1925, [vi], **49**, 1165; *A.*, ii, 811. [45] *Ibid.*, 1925, [vi], **50**, 879; *A.*, ii, 1079. [46] *J.*, 1925, **127**, 2316. [47] *Z. Elektrochem.*, 1916, **22**, 53; *A.*, 1916, ii, 422. [48] *Ibid.*, 1921, **27**, 511; *A.*, 1922, ii, 9. [49] *J.*, 1923, **123**, 3079.

[50] *Helv. Chim. Acta*, 1924, **7**, 324; *A.*, 1924, ii, 326. [51] *Compt. rend.*, 1925, **181**, 33; *A.*, ii, 812. [52] *Bull. Soc. chim.*, 1923, **33**, 576; *A.*, 1923, ii, 526. [53] *J.*, 1920, **117**, 183. [54] *Z. Elektrochem.*, 1923, **29**, 521; *A.*, 1924, ii, 10. [55] *Z. wiss. Photochem.*, 1924, **23**, 30; *A.*, 1924, i, 821. [56] R. G. W. Norrish and E. K. Rideal, *J.*, 1925, **127**, 787. [57] *Z. physikal. Chem.*, 1914, **86**, 564; *A.*, 1914, ii, 261. [58] *Z. wiss. Photochem.*, 1914, **13**, 383; *A.*, 1914, ii, 447. [59] *Z. physikal. Chem.*, 1922, **103**, 139; *A.*, 1923, ii, 50.

[60] *J.*, 1925, **127**, 822. [61] *J. Amer. Chem. Soc.*, 1923, **45**, 1210; *A.*, 1923, ii, 451. [62] *Z. wiss. Photochem.*, 1919, **18**, 231. [63] *Ibid.*, 1919, **19**, 22. [64] *Trans. Faraday Soc.*, March, 1926 (advance proof). [65] *Z. Elektrochem.*, 1914, **20**, 494; *A.*, 1915, ii, 205. [66] *Ibid.*, 1916, **22**, 202; *A.*, 1916, ii, 463. [67] *J. Amer. Chem. Soc.*, 1922, **44**, 2377; *A.*, 1923, ii, 22. [68] *J. Physical Chem.*, 1923, **27**, 74; *A.*, 1924, ii, 149. [69] *Z. wiss. Photochem.*, 1924, **23**, 66; *A.*, 1925, ii, 90.

[70] See, however, A. F. O. Germann, *J. Physical Chem.*, 1924, **28**, 1218. [71] *Z. physikal. Chem.*, 1920, **95**, 378; *A.*, 1920, ii, 615. [72] *Proc. Physical Soc.*, 1925, **37**, 287; *A.*, ii, 984. [73] *Z. physikal. Chem.*, 1923, **106**, 407; *A.*, 1923, ii, 813. [74] *Ibid.*, 1912, **79**, 141; *A.*, 1912, ii, 615. [75] *J. Physique*, 1913, **3**, 305. [76] *Z. wiss. Photochem.*, 1914, **14**, 196; *A.*, 1915, ii, 200. [77] *Ibid.*, 1915, **15**, 148, 183, 197; *A.*, 1916, ii, 68. [78] *Z. physikal. Chem.*, 1916, **91**, 722; *A.*, 1917, ii, 5. [79a] *Z. wiss. Photochem.*, 1905, **3**, 257. [79b] *Z. Elektrochem.*, 1908, **14**, 445.

[80] *Z. Elektrochem.*, 1920, **26**, 54; *A.*, 1920, ii, 210. [81] *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1918, 1228; *A.*, 1920, ii, 405. [82] *Ann. Physique*, 1919, [ix], **12**, 107; *A.*, 1920, ii, 3. [83a] *Z. physikal. Chem.*, 1922, **101**, 414; *A.*, 1922, ii, 605. [83b] *Ibid.*, 1922, **102**, 416; *A.*, 1923, ii, 3. [84] *Trans. Faraday*

Soc., 1924, **20**, 107; *A.*, 1925, ii, 56. [85] *J.*, 1924, **125**, 1233. [86] *J.*, 1925, **127**, 1026. [87] *Compt. rend.*, 1924, **178**, 697; *A.*, 1924, ii, 244. [88a] *Ibid.*, 1924, **179**, 52; *A.*, 1924, i, 929. [88b] *Ibid.*, p. 168; *A.*, 1924, ii, 719. [89] *Trans. Faraday Soc.*, March, 1926 (advance proof); *A.*, 1925, ii, 1074.

[90] *Z. Elektrochem.*, 1925, **31**, 350. [91] H. A. Taylor and W. C. M. Lewis, *J. Amer. Chem. Soc.*, 1924, **46**, 1606; *A.*, 1924, ii, 580. [92] N. S. Capper and J. K. Marsh, *ibid.*, 1925, **47**, 2847. [93] *Ibid.*, 1923, **45**, 1398; *A.*, 1923, ii, 527. [94] *J.*, 1921, **119**, 1948. [95] *Ann. Physique*, 1914, [ix], **2**, 5, 226; *A.*, 1915, ii, 123. [96] *J.*, 1914, **105**, 2065. [97] *Ann. Faculté Sci. Marseille*, 1915, **22**, 179; *A.*, 1915, ii, 828. [98] *J. Physique*, 1917, **7**, 10. [99] *Helv. Chim. Acta*, 1924, **7**, 307; *A.*, 1924, ii, 327.

[100] *J. Amer. Chem. Soc.*, 1909, **31**, 770; *A.*, 1909, ii, 632. [101] *Trans. Faraday Soc.*, March, 1926 (advance proof). [102] M. Padoa and N. Vita, *Gazzetta*, 1924, **54**, 147; *A.*, 1924, ii, 322. [103] *Compt. rend.*, 1923, **177**, 956; *A.*, 1923, ii, 815. [104] J. Vranek, *Z. Elektrochem.*, 1917, **23**, 336. [105] E. C. Hatt, *Z. physikal. Chem.*, 1918, **92**, 513; *A.*, 1918, ii, 143. [106] *Trans. Faraday Soc.*, March, 1926 (advance proof); *A.*, 1925, ii, 1078. [107] *Z. physikal. Chem.*, 1924, **114**, 208; *A.*, 1925, ii, 218. [108] *Trans. Faraday Soc.*, March, 1926 (advance proof); *A.*, 1925, ii, 1083. [109] O. Warburg and E. Negelein, *Z. physikal. Chem.*, 1923, **106**, 191; *A.*, 1923, ii, 718.

[110] *Ibid.*, 1924, **108**, 236; *A.*, 1924, ii, 329. [111] *Ann. Physique*, 1918, [ix], **10**, 133; *A.*, 1918, ii, 418. [112] *Phil. Mag.*, 1922, [vi], **43**, 757; *A.*, 1922, ii, 334. [113] *Z. Physik*, 1922, **10**, 176; *A.*, 1922, ii, 602. [114] *Ibid.*, 1923, **16**, 71; *A.*, 1923, ii, 528. [115] *J. Physical Chem.*, 1925, **29**, 926; *A.*, ii, 884. [116] P. F. Büchi, *Z. physikal. Chem.*, 1924, **111**, 269; *A.*, 1924, ii, 669. [117] E. Rudberg, *Z. Physik*, 1924, **24**, 247; *A.*, 1924, ii, 467. [118] J. Böeseken and W. D. Cohen, *Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 849; *A.*, 1915, ii, 37. [119] J. Plotnikov, *Z. wiss. Photochem.*, 1919, **19**, 40; *A.*, 1920, ii, 212.

[120] E. J. Bowen, *J.*, 1923, **123**, 1199. [121] A. Kailan, *Z. physikal. Chem.*, 1920, **95**, 215; *A.*, 1920, ii, 576. [122] W. T. Anderson, jun., and F. W. Robinson, *J. Amer. Chem. Soc.*, 1925, **47**, 718; *A.*, ii, 415. [123] E. K. Rideal and R. G. W. Norrish, *Proc. Roy. Soc.*, 1923, [*A*], **103**, 342; *A.*, 1923, ii, 362. [124] A. Benrath and A. Obladen, *Z. wiss. Photochem.*, 1922, **22**, 65; *A.*, 1922, ii, 731. [125] J. Plotnikov, *ibid.*, 1919, **19**, 1. [126] R. O. Griffith and W. J. Shutt, *J.*, 1923, **123**, 2752. [127] G. Kornfeld, *Z. wiss. Photochem.*, 1921, **21**, 66; *A.*, 1921, ii, 670. [128] J. Eggert and W. Borinski, *Physikal. Z.*, 1923, **24**, 504; *A.*, 1924, i, 368. [129] *Z. physikal. Chem.*, 1921, **98**, 94.

[130a, b] *Compt. rend.*, 1915, **160**, 440, 519; *A.*, 1915, ii, 329. [131] *Z. physikal. Chem.*, 1919, **93**, 721; *A.*, 1920, ii, 144. [132] *Z. wiss. Photochem.*, 1922, **21**, 117; *A.*, 1922, i, 419. [133] *Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 97; *A.*, 1915, ii, 719. [134] *Compt. rend.*, 1924, **178**, 708; *A.*, 1924, ii, 249. [135] *Physikal Z.*, 1906, **7**, 899. [136] L. Bruner and S. Czarnecki, *Bull. Acad. Sci. Cracow*, 1910, 516; *A.*, 1911, ii, 241. [137] *Trans. Faraday Soc.*, March, 1926 (advance proof); *A.*, 1925, ii, 1075. [138] *J.*, 1911, **99**, 1726. [139] *Gazzetta*, 1921, **51**, i, 193.

[140a, b] *J. Physical Chem.*, 1914, **18**, 166, 521; *A.*, 1914, ii, 255, 602. [141] *Trans. Faraday Soc.*, March, 1926 (advance proof); *A.*, 1925, ii, 1080. [142] *Gazzetta*, 1925, **55**, 87; *A.*, 1925, ii, 415. [143a] *J. Amer. Chem. Soc.*, 1920, **42**, 2506; *A.*, 1921, ii, 99. [143b] *Ibid.*, 1923, **45**, 2285; *A.*, 1923, ii, 813. [144] See also E. Baur, *Trans. Faraday Soc.*, March, 1926 (advance proof); *A.*, 1925, ii, 1082. [145] *Z. wiss. Photochem.*, 1922, **21**, 175. [146] *Helv. Chim. Acta*, 1918, **1**, 186; *A.*, 1918, ii, 284. [147] *Z. Elektrochem.*, 1922, **28**, 499; *A.*, 1923, ii, 109.

[148] *Ber.*, 1923, **56**, [*B*], 455; *A.*, 1923, ii, 205. [149] *Z. physikal. Chem.*, 1916, **91**, 347; *A.*, 1916, ii, 281.

[150] *J.*, 1907, **91**, 942. [151] *Ber.*, 1921, **54**, [*B*], 1148; *A.*, 1921, ii, 476. [152] R. O. Griffith and J. McWillie, *J.*, 1923, **123**, 2767. [153] H. von Halban and H. Geigel, *Z. physikal. Chem.*, 1920, **96**, 233; *A.*, 1921, ii, 147. [154] *Compt. rend.*, 1914, **158**, 32; *A.*, 1914, ii, 86. [155] *Z. physikal. Chem.*, 1913, **85**, 329; compare *A.*, 1913, ii, 819. [156] J. H. Mathews and R. V. Williamson, *J. Amer. Chem. Soc.*, 1923, **45**, 2574; *A.*, 1924, ii, 10. [157] A. Benrath, E. Hess, and A. Obladen, *Z. wiss. Photochem.*, 1922, **22**, 47; *A.*, 1922, ii, 731. [158] E. Baur and A. Rebmann, *Helv. Chim. Acta*, 1922, **5**, 221; *A.*, 1922, ii, 337. [159] *J. Amer. Chem. Soc.*, 1923, **45**, 650; *A.*, 1923, ii, 278.

[160] *Rec. trav. chim.*, 1916, **36**, 117; *A.*, 1916, ii, 592. [161] *Ber.*, 1916, **49**, 1366; *A.*, 1916, ii, 546. [162] *Monatsh.*, 1918, **39**, 241; *A.*, 1918, ii, 385. [163] *Z. wiss. Photochem.*, 1920, **20**, 57; *A.*, 1921, ii, 76. [164] *Ibid.*, p. 206; *A.*, 1921, ii, 291. [165] *Z. physikal. Chem.*, 1921, **97**, 426; *A.*, 1921, ii, 365. [166] *Trans. Faraday Soc.*, March, 1926 (advance proof); *A.*, 1925, ii, 1082. [167] R. Stoermer, *Ber.*, 1914, **47**, 1786, 1793, 1795; *A.*, 1914, i, 925, 962, 964. [168] H. Stobbe, *ibid.*, 1919, **52**, 666; *A.*, 1919, i, 273. [169] *Z. physikal. Chem.*, 1914, **87**, 333; *A.*, 1914, ii, 449.

[170] *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1919, 960; *A.*, 1920, ii, 405. [171] H. Stobbe, *J. pr. Chem.*, 1914, [ii], **90**, 277; *A.*, 1915, i, 261. [172] W. T. Anderson, jun., *J. Amer. Chem. Soc.*, 1924, **46**, 797; *A.*, 1924, ii, 408. [173] C. Winther, *Danske Vid. Selsk. Math. Phys. Medd.*, 1920, **2**, No. 1; *A.*, 1920, ii, 426. Compare W. Kistiakowsky, *Z. physikal. Chem.*, 1900, **35**, 431. [174] J. C. Ghosh and J. Mukherjee, *J. Indian Chem. Soc.*, 1925, **2**, 165; *A.* ii, 1179. [175] W. Gallenkamp, *Chem. Ztg.*, 1916, **40**, 235; *A.*, 1916, ii, 207. [176] L. Pusch, *Z. Elektrochem.*, 1918, **24**, 336; *A.*, 1919, ii, 208. [177] W. Nernst, *ibid.*, p. 335; *A.*, 1919, ii, 208. [178] A. J. Allmand, *Trans. Faraday Soc.*, March, 1926 (advance proof); *A.*, 1925, ii, 1074. [179] *Z. physikal. Chem.*, 1924, **111**, 315; *A.*, 1924, ii, 669. See also E. Staechelin, *ibid.*, 1920, **94**, 542; *A.*, 1920, ii, 580.

[180] *Z. Elektrochem.*, 1921, **27**, 133. [181] *J. Ind. Eng. Chem.*, 1924, **16**, 270. [182] *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1923, 110; *A.*, 1923, ii, 526. [183] *Ann. Physique*, 1919, [ix], **11**, 6; *A.*, 1919, ii, 177. [184] *Danske. Vid. Selsk. Math. Phys. Medd.*, 1920, **2**, No. 3; *A.*, 1920, ii, 404. [185] *Z. Physik*, 1923, **14**, 383; *A.*, 1923, ii, 361. [186a] *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1914, 872; *A.*, 1920, ii, 404. [186b] *Ibid.*, 1916, 314; *A.*, 1920, ii, 405. [186c] *Ibid.*, 1918, 300; *A.*, 1920, ii, 405. [187] [With H. Hartley, W. D. Scott, and H. G. Watts], *J.*, 1924, **125**, 1218. [188] *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1923, 116; *A.*, 1923, ii, 526. [189] *Proc. Roy. Soc.*, 1923, [*A*], **103**, 366; *A.*, 1923, ii, 452.

[190] *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1921, 641; *A.*, 1922, ii, 10. [191] F. Weigert and L. Brodmann, *Trans. Faraday Soc.*, March, 1926 (advance proof); *A.*, 1925, ii, 1075. [192] *Ibid.*, March, 1926 (advance proof); *A.*, 1925, ii, 1074. [193a] *Z. wiss. Photochem.*, 1922, **21**, 134; *A.*, 1922, ii, 248. [193b] *Ibid.*, 1923, **22**, 110; *A.*, 1923, ii, 451. [194] *Physikal. Z.*, 1920, **21**, 602. [195] *Z. wiss. Photochem.*, 1920, **19**, 275; *A.*, 1920, ii, 461. [196] *Ann. Physik*, 1925, [iv], **76**, 225; *A.*, ii, 365; *Z. Physik*, 1925, **31**, 411; *A.*, ii, 266. [197] *Trans. Faraday Soc.*, March, 1926 (advance proof); *A.*, 1925, ii, 1077. [198] *Z. Elektrochem.*, 1915, **21**, 113; *A.*, 1915, ii, 813. [199] *Z. Physik*, 1921, **5**, 410.

[200a, b] *Physikal. Z.*, 1908, **9**, 889, 894; *A.*, 1909, ii, 106, 109. [201] *Z. Elektrochem.*, 1925, **31**, 343. [202] A. J. Allmand, *Trans. Faraday Soc.*, March, 1926 (advance proof); *A.*, 1925, ii, 1079. [203] *Z. Physik*, 1921, **4**, 89; compare

A., 1922, ii, 728. [204] *Physical Rev.*, 1924, [ii], **23**, 693; *A.*, 1924, ii, 509. [205] *Z. physikal. Chem.*, 1915, **90**, 385; *A.*, 1916, ii, 9. [206] *Proc. Roy. Soc. Edinburgh*, 1924, **44**, 197; *A.*, 1925, ii, 470. [207] *Z. physikal. Chem.*, 1922, **100**, 566; *A.*, 1922, ii, 336. [208] *E. g.*, R. W. Wood and J. Franck, *Physikal. Z.*, 1911, **12**, 81; compare *A.*, 1911, ii, 169; R. W. Wood, *ibid.*, 1912, **13**, 353; R. W. Wood and W. P. Speas, *ibid.*, 1914, **15**, 317; *A.*, 1914, ii, 233. [209] *Z. Elektrochem.*, 1917, **23**, 357; *A.*, 1918, ii, 50; *Z. Physik*, 1919, **21**, 623, and subsequent papers.

[210] *E. g.*, J. Franck and G. Hertz, *Physikal. Z.*, 1919, **20**, 132; *A.*, 1919, ii, 206. [211] *Z. Physik*, 1921, **4**, 46; *A.*, 1921, ii, 291. [212] *Ibid.*, 1922, **9**, 259; *A.*, 1922, ii, 464. [213] *Trans. Faraday Soc.*, March, 1926 (advance proof); *A.*, 1925, ii, 1026. [214] *J.*, 1921, **119**, 1025. [215] *Z. physikal. Chem.*, 1924, **108**, 118; *A.*, 1924, ii, 213. [216] *Trans. Faraday Soc.*, March, 1926 (advance proof); *A.*, 1925, ii, 1078. [217] J. A. Christiansen and H. A. Kramers, *Z. physikal. Chem.*, 1923, **104**, 451; *A.*, 1924, ii, 28. [218] J. A. Christiansen, *ibid.*, 1922, **103**, 99; *A.*, 1923, ii, 62. [219] *Ibid.*, 1913, **85**, 297; *A.*, 1913, ii, 1039.

[220] *Trans. Faraday Soc.*, March, 1926 (advance proof); *A.*, 1925, ii, 1080.

INDEX OF AUTHORS' NAMES

Aarflot, H., 192.
Abel, 223.
Abonnenc, L., 326, 329.
Acree, S. F., 124.
Adair, G. S., 238, 314.
Adam, H. R., 192.
Adam, N. K., 23, 26, 27, 81, 318, 319, 323, 331.
Adams, E. W., 69.
Adkins, H., 21, 69, 72, 330.
Adler, 222.
Adolf, M., 313.
Adova, A. N., 307.
Agte, K., 293.
Albrecht, W. A., 207.
Alexander, J., 282.
Allan, J., 78.
Allen, C. F. H., 135.
Allen, E., 222, 223.
Allmand, A. J., 41, 338, 372.
Alphen, J. van, 158.
Alsterberg, G., 180.
Alterthum, H., 54.
Amberger, K., 79.
Ambler, H. R., 181.
Ambrus, R., 68.
Aminoff, G., 277, 279.
Anargyros, A., 287.
Anderegg, F. O., 312.
Anderson, W. T., jun., 338, 347, 350, 356, 366, 371, 372
André, G., 215.
Andreanelli, M., 301.
Andrew, G. W., 22.
Andrich, 339, 340, 350.
Angelescu, B. N., 174.
Anschutz, R., 109.
Anselm, F., 134.
Anson, 237, 238.
Anthony, J. D. C., 28.
Appenrodt, J., 126.
Ardagh, E. G. R., 173.
Arkel, A. E. van, 56, 57.
Armstrong, A. H., 256.
Armstrong, E. F., 19, 20, 22, 78, 79, 89.
Arnold, 227.
Arrhenius, O., 205.
Asahara, G., 52.
Asbury, W. C., 18.
Ascherl, A., 73.
Aston, F. W., 46, 48.
Atterberg, A., 132.
Aubel, 231.
Audubert, R., 293, 302.
Auerbach, R., 295, 298.
Auger, V., 51.
Auwers, K. von, 106, 107, 109, 158, 160, 161, 162, 163, 165, 166, 167.
Ayyar, P. R., 67.
Azuma, R., 41.

Bach, 175, 235.
Bacher, F., 109.
Bachmann, W., 320.
Baeyer, A. von, 121.
Bahl, D. C., 299.
Bahr, T., 166, 167.
Bailar, J. C., 58.
Bailly, O., 186.
Baker, H. B., 47, 349, 369.
Baker, J. L., 93.
Baker, J. W., 129, 130.
Baker, S., 84.
Balareff, D., 293.
Balks, R., 206.
Baly, E. C. C., 47, 337, 343, 366.
Balz, P., 65.
Bancroft, W. D., 17, 281, 327, 354.
Banerji, R. C., 370.
Bangham, D. H., 327, 328, 329.
Bangler, B., 138.
Banik, 239.
Bappert, R., 134.
Barbier, P., 121.
Barclay, E. H., 331.
Bardet, J., 56.
Bardwell, D. C., 47, 275.
Barger, G., 154.
Barkas, W. W., 291.
Barker, 337, 343.
Barnett, L. H., 260.
Bartell, F. E., 332.
Bartunek, R., 99.
Basu, S. K., 300.
Batelli, 230.
Batuecas, T., 43, 44.
Bauch, J., 79.
Baude, 218.
Baur, E., 336, 348, 354, 359, 371, 372.
Baxter, W. P., 31, 33.

Bayer, J., 107.
Bayer, O., 153.
Bayley, C. H., 21.
Bechhold, H., 296, 297.
Beck, W., 304.
Beckmann, E., 107, 123.
Bédowé, J., 69.
Beebe, R. A., 19.
Beekley, J. S., 331.
Beling, R. W., 201.
Bell, J. M., 45.
Bellenot, 342, 343, 347, 353, 355, 367.
Beller, H., 133.
Benedicks, C., 251.
Bengough, G. D., 48.
Benoit, F., 175.
Benrath, A., 336, 337, 338, 350, 371, 372.
Berg, O., 63.
Berg, O. W., 46.
Bergheimer, E., 179.
Berglund, V., 56.
Bergman, M., 87.
Bergstrom, F. W., 64.
Berl, E., 330.
Bernhardt, H., 172.
Bernhauer, E., 152.
Bernton, A. W., 127.
Berry, J. H., 330.
Berthelot, 53, 341, 347, 348, 353.
Berthoud, 337, 342, 343, 345, 347, 353, 355, 358, 367.
Bertolo, P., 183.
Bertram, J., 132.
Bettzieche, F., 116.
Beuker, H., 53.
Bezssonov, 219.
Bhagwat, V. K., 156.
Bhatnagar, S. S., 299.
Bikerman, J. J., 289.
Biltz, H., 190.
Biltz, W., 60, 309.
Binder, K., 170.
Bingham, E. C., 295.
Binkert, A., 125.
Birckenbach, L., 63.
Birtwell, C., 102.
Bischoff, F., 330.
Bishop, 220.
Bishop, G., 106, 107, 108.
Bittner, K., 179.
Bizzell, J. A., 207.
Black, A., 216, 217, 218.
Black, A. P., 75.
Blaise, E. E., 135.
Blanchetière, A., 312.
Blanck, E., 196, 205.
Blench, E. A., 20.
Blencke, W., 51.
Blicke, F. F., 124, 125, 126.
Blindow, K., 136.
Blüh, O., 35.
Bobko, E. W., 204.
Bode, K., 44.
Bodenstein, M., 12, 13, 15, 17, 20, 62, 335, 337, 338, 343, 347, 349, 355, 356, 359, 360, 366, 367, 368, 369.
Böeseken, J., 77, 79, 108, 109, 371.
Böhme, E., 306.
Boer, J. H. de, 56, 57.
Boeters, H., 287.
Böttcher, 144.
Bogue, R. H., 305, 308.
Bokorny, T., 211.
Bolin, 347.
Boll, 341, 348, 349, 353, 355.
Bollenbeck, K., 201.
Bonath, K., 144.
Bone, W. A., 22.
Bonhoeffer, 335, 337, 355.
Book, 337, 355.
Boomer, E. H., 46.
Booth, H., 62, 335.
Borinski, W., 355, 371.
Born, M., 15, 35, 359.
Bornträger, A., 182.
Borsook, 234.
Bossuet, R., 189.
Boswell, M. C., 21.
Bottini, E., 206.
Bougault, 80.
Bourguel, M., 75.
Boutaric, A., 300.
Bowen, A. R., 79.
Bowen, E. J., 62, 335, 337, 340, 341, 355, 356, 358, 368, 371.
Bowen, N. L., 269.
Bozorth, R. M., 248, 257.
Bradfield, 194, 203.
Bradley, A. J., 63, 252, 253.
Brady, O. L., 106, 107, 108, 109, 110.
Bragg, (Sir) W. H., 242.
Bragg, W. L., 257, 258.
Brandt, A., 50.
Braun, J. von, 121, 153, 163.
Bredig, G., 54, 369.
Brenchley, (Miss) W. E., 210.
Brennen, H., 45.
Brieger, C., 320.
Briggs, G. E., 233.
Briggs, S. H. C., 65.
Brill, R., 245.
Brillouin, 321.
Brinton, P. H. M. P., 176, 177.
Briscoe, H. V. A., 43, 45.
Britton, H. T. S., 172.
Brode, W. R., 188.
Brodmann, L., 356, 372.
Brönsted, J. N., 29, 30, 32.
Brosche, A., 61.
Broughall, G. M., 173.
Brown, 93.
Brown, F. S., 290.
Bruchhausen, F. von, 148, 150.

Bruckner, B., 296.
Brudi, E., 133.
Brünnich, J. C., 191.
Brugsch, 223.
Bruhl, A., 174.
Bruner, L., 371.
Brunner, K., 155.
Brunner, O., 142, 153.
Bruylants, P., 44.
Bucherer, H., 106.
Buck, J. S., 145.
Büchi, P. F., 355, 371.
Bülow, C., 186.
Buhlea, C., 144.
Bukschnewski, J. D., 188.
Bundesmann, H., 106.
Burian, O., 206.
Burk, R. E., 12, 22.
Burr, 220, 223.
Burrows, G. J., 113.
Burt, F. P., 328, 329.
Burt, R. C., 48.
Burtles, R., 157.
Burton, E. F., 292.
Burton, J. Q., 178.
Bury, C. R., 290.
Busch, M., 111.
Busch, W., 49.
Busche, M., 164.
Buston, H. W., 104.
Butironi, 337, 347.
Butler, J. A. V., 38, 39.
Buttgenbach, H., 276, 277.
Buzagh, A. von, 316.
Bylinkin, I. G., 138.

Cahen, 229.
Calcott, W. S., 185.
Callan, T., 183.
Callow, E. H., 232, 233, 309.
Campbell, A. N., 41.
Campbell, R., 275.
Camps, R., 139.
Canneri, G., 176.
Cantoni, O., 175.
Capper, N. S., 371.
Carey, R. M., 60.
Cario, G., 13, 334.
Carlton, (Miss) M., 47, 50, 349, 369.
Carman, 220.
Caro, R. J., 178.
Carobbi, G., 277, 278.
Carré, M. H., 96, 213.
Carrière, J. F., 325.
Carver, E. K., 319.
Cary, A., 26, 27, 324.
Carson, C. M., 188.
Caspar, J., 121.
Cathala, 337, 343, 345, 358, 368, 349.
Cattelain, E., 171.
Cavanagh, B. A. M., 30.
Chabot, G., 170.
Chadwick, 349.
Chamberlin, D. S., 180.
Chambers, R. F., 184.
Channon, 218, 219.
Chapin, R. M., 317.
Chapman, A. W., 114.
Chapman, D. L., 336, 337, 343, 345, 347, 349, 353, 367, 369.
Chapman, M. C. C., 336, 337, 343, 345, 349, 367.
Charlton, J., 204.
Charonnat, R., 65.
Chatterji, A. C., 310.
Chavaux, 80.
Chem. Fabrik auf Aktien (vorm. E. Schering), 138.
Cheramy, P., 186.
Chick, (Miss), 216.
Child, W. C., 72.
Chirvinsky, P. N., 261.
Chodat, F., 235, 314.
Christiani-Kronwald, A., 174.
Christiansen, J. A., 11, 12, 14, 56, 373.
Ciamician, G., 118.
Cikrtová, M., 177.
Claisen, L., 125.
Clark, B. L., 309.
Clark, E. P., 221, 231.
Clark, G. L., 18, 322.
Clark, N. A., 211.
Clarke, B. L., 52.
Clarke, F. W., 259, 261.
Classen, A., 46.
Clemens, F., 64.
Clemo, G. R., 141.
Clerici, E., 189.
Clewer, 81.
Clewer, H. W. B., 135.
Clibbens, D. A., 102, 187.
Clutterbuck, 229.
Coehn, A., 17, 47, 337, 339, 341, 349, 351, 359, 368, 370.
Cohen, 231.
Cohen, W. D., 371.
Cohn, E. J., 313.
Colani, A., 169.
Colin, H., 212
Collander, R., 297.
Collins, G. E., 99.
Collip, 221.
Compton, K. T., 39.
Conant, 238.
Conduché, A., 165.
Congdon, L. A., 174, 175.
Constable, F. H., 20.
Cooper, S. R., 169.
Corey, R. B., 54.
Correns, E., 107.
Costa, D., 330.
Costa, J. L., 42.
Coster, D., 189.

Coutts, J. R. H., 291.
Coward, 217, 218, 219.
Cox, D. C., 191.
Crittenden, E. D., 18.
Cross, C. F., 98.
Crowther, E. M., 205.
Csapó, J., 304.
Cunliffe, 338.
Currie, J. E., 292.
Curtis, 335, 347, 350.
Curtman, L. J., 169.
Cybulski, 134.
Czarnecki, S., 371.
Czochralski, J., 251.

Dakin, 229.
Dale, 223.
Daniels, 341.
Daniels, F., 16, 38, 58, 370.
Dannerth, G. A., 191.
Daubenspeck, G. W., 312.
Dauvillier, A., 248.
David, L., 183.
David, W. T., 14.
Davies, C. W., 37.
Davis, A. R., 213.
Debye, P., 30, 31, 35, 36.
Decker, H., 145.
Decker, M., 295.
Dede, L., 286.
Dehnert, F., 99.
Delaby, R., 68.
Delbrück, K., 88.
Demolon, A., 196.
Demoussy, E., 215.
Dencke, H., 176.
Denigès, G., 173, 189.
Dennis, L. M., 54, 55, 175.
Dennler, W. S., 116.
Densch, A., 204, 210, 211.
Desgrez, A., 184.
Desvergnes, L., 188.
Dhar, N. R., 297, 303, 310, 318, 335, 336, 343, 344, 347.
D'Huart, 328.
Diamant, N., 144.
Dickens, F., 129, 222.
Dickinson, R. G., 369.
Diepolder, E., 142.
Dijkstra, D. W., 44.
Dimitrov, M., 171.
Dingemanse, E., 332.
Dirken, M. N. J., 180.
Dirsch, R., 70.
Dirska, G., 64.
Dixon, 226.
Dobrowsky, A., 150.
Dodds, 222.
Dokan, S., 281.
Doisy, 222.
Dojmi, S., 203.
Dolejšek, V., 41, 64.
Dominicis, A. de, 203.
Donnan, F. G., 23, 41.
Doolan, J. J., 302.
Dorée, C., 98.
Dorenfeldt, (Mme.), 46.
Doser, A., 86.
Doughty, H. W., 75, 177.
Dowding, E. S., 215.
Drew, H. D. K., 73.
Driggs, F. H., 45.
Drinker, P., 293.
Druce, J. G. F., 64.
Drummond, 217, 218, 219.
Druschinin, D. W., 204.
Dschu, G. L., 151
Duane, W., 256.
Dubois, R., 186.
Duchon, E., 210.
Duckers, G. E., 283.
Duclaux, J., 296.
Dudley, 239.
Dumanski, A., 291.
Dunn, P. 109.
Duschinsky, R., 151.
Dushman, S., 16.
Dux, W., 17, 368.
Dyckerhoff, K., 118.
Dyer, J. W. W., 26, 81.

Eakle, A. S., 277.
Ebel, F., 77, 108, 109.
Eberman, N. F., 331.
Eberstaller, H., 142.
Eckert, 350.
Edser, E., 24.
Effront, J., 309.
Eggert, J., 355, 371.
Eibner, A., 82.
Eichelberger, L., 76.
Einhorn, A., 133.
Einstein, 333.
Ekkert, L., 170, 183.
Elam, C. F., 249, 251.
Eller, W., 206.
Ellis, G. W., 82.
Embden, 224, 225.
Emeléus, H. J., 59.
Emmerling, 231.
Emmett, P. H., 252.
Emschwiller, 341.
Emster, K. van, 114.
Endres, R., 70.
Engelstad, A., 98.
Engler, C., 117.
English, F. L., 185.
Erben, F., 144.
Errera, J., 296.
Estill, 224.
Ettisch, G., 304.
Ettisch, M., 250.
Euler, von, 350.
Evans, 220.
Evans, B. S., 174.
Evans, D. C., 51, 171.

Evers, F., 289.
Evers, N., 183.
Ewing, 338.
Eynon, L., 187.

Fajans, K., 20, 35, 54, 257, 348, 359.
Fanselow, J. R., 305.
Farrow, F. D., 320.
Faust, T. H., 188.
Fedorov, E. S. von, 240, 268.
Féher, D., 206.
Fehse, W., 54.
Feick, R., 291.
Feigl, F., 168, 172, 174.
Feist, K., 151.
Feller, 338.
Fells, H. A., 330.
Fenwick, F., 191.
Ferguson, A., 37.
Ferguson, W. C., 191.
Fernandes, L., 176.
Fersman, A. E., 259, 260, 278.
Feuchter, H., 309.
Field, E., 60.
Fieser, L. F., 181, 238.
Finger, H., 139.
Fink, H., 134.
Fiore, O. de, 277.
Firth, J. B., 330.
Fischenich, M., 314.
Fischer, A., 233.
Fischer, E., 87, 88, 89, 107.
Fischer, F., 206.
Fischer, H., 50, 133.
Fischer, O., 142, 143.
Fischer, W. M., 311.
Fleetwood, J. R., 204.
Fleissner, 144.
Fleury, P., 187.
Fleysher, M. H., 28, 192.
Flörov, K. W., 327.
Foerster, F., 61.
Forbes, 342.
Forcrand, De, 47.
Foresti, B., 19, 330.
Forstmann, W., 287.
Forsyth, R., 145.
Forsyth, W. G., 156.
Foshag, W. F., 277.
Fosse, R., 182, 186.
Fouard, E., 189, 296.
Fourneau, E., 172.
Fowler, R. H., 33.
Fox, 218.
Fränkel, S., 144, 222.
Francis, A. G., 181.
Francis, W., 207.
Franck, 334, 341, 359, 361, 362, 364.
Franck, J., 13, 15, 373.
François, M., 185.
Frankenstein, W., 117.
Franz, R., 109.
Frazer, J. E., 37.
Frederick, R. C., 179.
Frese, E., 161, 166, 167.
Freudenberg, K., 86, 161.
Freundlich, H., 291, 292, 300, 303, 308, 317.
Frey, A., 292.
Frey, H., 126.
Fricke, R., 51, 175, 309.
Fried, E., 284.
Friedel, E., 255.
Friedel, G., 143.
Friedenberger, G., 111.
Friederich, E., 58.
Friend, J. N., 180.
Fries, F. A., 71.
Frivold, A., 30.
Frölich, P. K., 190.
Fromm, E., 163.
Frumkin, A., 323, 324, 326.
Fuchs, L., 288.
Fujita, A., 295.
Funk, 220.
Funk, H., 177.
Furman, N. H., 176.

Gabriel, S., 164.
Gadamer, J., 148, 151, 152.
Gage, R. B., 277, 278.
Gaigailian, 161.
Galecki, A., 288.
Gall, H., 66.
Galley, R., 199.
Gallenkamp, W., 372
Gammal, C. A., 69.
Ganssen, R., 195, 201.
Garard, I. D., 283.
Gardner, 218.
Garner, W. E., 14, 20.
Gaschler, A., 49.
Gatti, U., 73.
Gauger, A. W., 19, 20, 21.
Gavrilov, N. N., 285.
Gay, L., 318.
Geake, A., 187.
Gebhardt, H., 174.
Gedroiz, K. K., 194, 197, 198, 199, 202.
Gee, 347.
Gehring, A., 205.
Geiger, H., 372.
Geiling, 223.
Gelbach, R. W., 28.
Georgian, N., 173.
Gerlach, H., 49, 65.
Gerlach, M., 207.
Germann, A. F. O., 370.
Gessner, H., 199.
Getz, D., 170.
Ghigliotto, C., 182.
Ghosh, B. N., 303.
Ghosh, J. C., 36, 372.
Ghosh, S., 303.

Gibbs, H. D., 231.
Gibbs, R. E., 242, 255.
Giemsa, G., 144.
Giesy, P. M., 284.
Gilbert, E. C., 192.
Gilbert, H. W., 324.
Gilchrist, H. S., 87.
Gile, 210.
Gilman, H., 75, 183.
Girard, A., 172.
Glasstone, S., 193.
Glattfield, J. W. E., 75.
Gleditsch, (Mlle.) E., 44, 46.
Glocker, R., 248, 251.
Goard, A. K., 24, 26, 322, 326.
Godden, W., 178.
Godnow, T. N., 133.
Göhring, 337, 338, 349, 358.
Goldberg, W., 60.
Goldberger, A. von, 335, 370.
Goldschmidt, S., 70.
Goldschmidt, V., 262.
Gombos, H., 189.
Gonell, H. W., 245, 246, 247.
González, A., 75.
González, F., 45.
Goode, K. G., 191.
Goodson, J. A., 135.
Gorbatschev, A., 326.
Gordon, 232, 233.
Gordon, S. G., 267.
Gortner, R. A., 235, 296, 312.
Goss, F. R., 109.
Gossner, B., 263, 267.
Gottschalk, 225.
Graaff, de, 231.
Graf, F., 103.
Grafe, V., 213.
Grafton, E. H., 24.
Granacher, C., 164.
Grandadam, 48.
Green, R. G., 323.
Greenwood, C. V., 308.
Greider, C. E., 328.
Greig, J. W., 269, 271.
Griffith, R. O., 17, 341, 348, 349, 371, 372.
Griffiths, J. P., 110.
Grignard, N., 121.
Gross, P., 30, 31, 35.
Gross, R., 251.
Grotrian, 361.
Grüss, 335, 337, 338, 355, 361.
Grundmann, W., 284.
Guckel, M., 54.
Günther, P., 189.
Guest, H. H., 68.
Gulland, J. M., 139.
Guntz, A., 175.
Gupta, S. R. D., 305.
Guss, A. B., 174.
Gutbier, W., 285.
Gutmann, A., 164.
Hägglund, E., 98.
Haerdi, W., 130.
Hafner, E. A., 35.
Hagene, P., 186.
Hahn, F. L., 170, 172, 173, 175.
Hahn, F. V. von, 286, 293.
Haidinger, W., 275.
Haken, W., 55.
Halban, H. von, 372.
Haldane, 233.
Hall, A. D., 198.
Hall, L., 98.
Hallimond, A. F., 264.
Halpern, O., 30, 31, 35.
Halvorson, H. O., 323.
Hamer, (Miss) F. M., 144.
Hammett, L. P., 169.
Handy, 218.
Hantzsch, A., 58, 162.
Happold, 235.
Hara, R., 54.
Hardy, (Sir) W., 27, 323.
Harington, 221.
Harkins, W. D., 24, 322, 325.
Harnack, 157.
Harned, H. S., 13, 28, 30.
Harries, C., 160.
Harris, 227.
Harris, L. J., 313.
Harteck, P., 62, 335.
Hartley, H., 28, 33, 37, 67.
Hartmann, W., 176.
Hartong, B. D., 191.
Hartree, D. R., 258.
Harvey, C. O., 177.
Harvey, E. H., 295, 309.
Harvey, W. G., 49.
Hasche, R. L., 57.
Hatschek, E., 281, 289, 298, 309, 317.
Hatt, E. C., 352, 355, 371.
Havighurst, R. J., 256.
Haworth, R. D., 147, 148, 151.
Haworth, W. N., 83, 84.
Haynes, D., 96.
Headdon, W. P., 273.
Heczko, T., 174.
Hedestrand, G., 27.
Hedvall, J. A., 62.
Heffter, 227.
Heilingötter, R., 175.
Heilmann, R., 160.
Heilmann, S., 118.
Helbig, D., 57.
Helferich, B., 71, 87.
Heller, 139.
Heller, G., 162.
Helman, 217.
Hendrixson, W. S., 178.
Hendry, J. L., 313.
Henri, 339, 349.
Hennings, A. E., 39.
Hensle, A., 125.

Hentschel, 252.
Henwood, A., 60.
Herboth, L., 170.
Herbst, H., 329, 332.
Hermann, 222.
Herschmann, O., 144.
Hertel, 337, 338.
Hertz, G., 373.
Herzberg, G., 196.
Herzog, R. O., 100, 243, 244, 245, 246, 247, 294.
Heslinga, J., 184.
Hess, A. F., 216, 217.
Hess, E., 372.
Hess, K., 100, 101, 102, 122, 134, 187.
Hesse, 234.
Heukelekian, H., 207.
Heumann, J., 288.
Heuser, E., 99.
Hevesy, G., 45, 56.
Heymann, E., 295.
Heyrovský, J., 40, 41, 64, 190.
Heyse, M., 133.
Hibbert, E., 187.
Hicks, 222.
Hieulle, A., 182.
Hildebrand, J. H., 37, 38.
Hilditch, T. P., 19, 20, 22, 78, 79.
Hill, 216, 341, 340, 344.
Hinshelwood, C. N., 12, 14, 16, 22, 23.
Hirst, E. L., 83, 84, 101.
Hirst, H. S., 16, 58.
Hissink, D. J., 201, 202.
Hitchcock, D. L., 315.
Hjort, 221.
Hoagland, D. R., 213.
Hobson, R. P., 209.
Hock, A., 193, 204.
Höfchen, 143.
Hönigschmid, O., 43, 45, 48.
Hoeven, C. van der, 187.
Hoff, W., 201.
Hoffman, W. F., 296, 312.
Hohlfeld, E., 329.
Holben, F. J., 184.
Holboll, 224.
Holden, 224.
Holden, E. F., 272.
Holmberg, B., 128.
Holmes, E., 81.
Holmes, W. C., 188.
Hooper, D., 186.
Hopkins, B. S., 45.
Hopkins, (Sir) G., 225, 226.
Horsters, 223.
Horton, L., 129.
Horvat, V., 213.
Hout, M. A. H. van den, 187.
Hovorka, F., 32, 319.
Howe, 65.
Hudig, J., 201.
Hudleston, L. J., 28.
Hudson, 88.
Hückel, E., 30, 31, 33, 35, 36, 41, 288, 314.
Hütz, H., 107.
Hughes, J., 12.
Huldchinsky, 216.
Hume, 216.
Hume, J., 50.
Humphreys, R. W., 84.
Hummis, 204, 211.
Hunt, J. K., 16, 58.
Hurd, C. D., 73.
Hurst, W. W., 21.
Hurtley, 229.
Husson, A., 19.
Hyden, W. L., 316.

Iljin, B., 327.
Imker, A., 55.
Ing, H. R., 127, 128.
Ingersoll, L. R., 256.
Ingold, C. K., 109, 110, 126, 129.
Iredale, T., 24, 26.
Irvine, (Sir) J. C., 85, 95, 101.
Ivanov, D., 75.
Ivanov, N. N., 212.

Jabłczyński, K., 302, 303.
Jackson, 236.
Jacob, P., 138.
Jacquet, D., 153.
Jaeger, F. M., 44.
Jaeger, G., 170.
Järvinen, K. K., 174.
Jakob, W. F., 174, 175.
Jancke, W., 243.
Jander, G., 175.
James, R. W., 252.
Javillier, 218.
Jenks, C. A., 38.
Jessop, G., 318, 321.
Jílek, A., 172, 190.
Job, 341.
Jobst, G., 291.
Jodidi, S. L., 212.
Joffe, 351.
Johansson, K., 277.
Johlin, J. M., 325.
John, H., 140.
Johnsen, A., 274.
Johnson, E. B., 175.
Johnson, F. M. G., 330.
Johnston, 222, 341.
Johnston, E. H., 15, 370.
Johnston, J. H. S., 305, 323.
Jolibois, P., 189.
Jones, D. C., 330, 338, 353.
Jones, R. M., 178.
Jones, W., 236, 237.
Joos, G., 257.
Jordan, O., 106.
Jorgensen, G., 178.
Jünger, A., 87.
Jung, 337, 341, 359, 368.

Jung, G., 17, 370.
Justin-Mueller, 307.

Kadesch, W. H., 39.
Kahlenberg, H. H., 51.
Kailan, A., 352, 371.
Kaiser, F., 160.
Kalb, L., 107.
Kalle, K., 82.
Kameyama, N., 41, 314.
Kamm, O., 125.
Kamm, W. F., 125.
Kanô, N., 171.
Kao, C. H., 61, 62, 178.
Kappen, H., 201, 205.
Kar, S. C., 25.
Karrer, P., 134, 164.
Karrer, S., 16.
Kaston, E., 100.
Katz, J. R., 100, 245.
Katzman, V. B. de, 136.
Kauffmann, M., 61.
Kaufmann, A., 143.
Kaufmann, H. P., 70.
Kaupp, 248.
Kautsky, H., 196, 364.
Kautter, T., 285.
Kawakami, 219.
Keesom, W. H., 251.
Keilin, 238.
Keiser, E., 326.
Kelber, C., 21.
Kellermann, K., 63, 337, 338, 353, 367.
Kelly, C. I., 145.
Kelly, M. W., 306.
Kelly, W. J., 293.
Kendall, J., 52.
Kermack, W. O., 153, 301, 302, 304.
Keschan, A., 169.
Kessler, S., 160.
Keunecke, E., 60.
Kiesel, A., 212.
Kimura, K., 56.
Kindscher, E., 175.
King, J., 323.
Kingsbury, F. L., 182.
Kinkel, E., 307.
Kinoshita, K., 278.
Kirschbaum, G., 121.
Kirste, H., 205.
Kistiakowski, G., 356, 369
Kitasato, 219.
Klages, A., 117.
Klason, P., 98.
Klein, O., 13, 364.
Klever, H. W., 118.
Klingstedt, F. W., 187.
Klockmann, P. K., 109.
Klosky, S., 309.
Knaggs, I. E., 256.
Knecht, E., 187.
Knoevenagel, E., 135.
Knoll, W., 100.
Knoop, 229.
Koblic, O., 176.
Köhler, K., 136.
Köhler, W., 162.
König, F., 329.
König, J., 66.
König, W., 99, 143.
Koenigs, E., 136.
Köster, H., 71.
Kofler, L., 295.
Kohler, E. P., 135, 165.
Kohlbrausch, 36.
Kohn, C. A., 125.
Kohn, H., 54.
Kollo, C., 173.
Kolthoff, I. M., 171, 180, 182, 191, 192, 284, 312.
Kondo, K., 314.
Konobejewski, S., 250.
Konsuloff, S., 211.
Kopaczewski, W., 283, 295, 309, 320.
Koppenhöfer, S., 133.
Korán, V., 321.
Korber, F., 251.
Kores, H. J., 317.
Kornfeld, G., 337, 343, 348, 353, 355, 356, 366, 367, 371.
Kossel, W., 257.
Kostyleva, E. E., 278.
Kouperman, 341.
Kôzu, S., 278.
Kraemer, E. O., 294, 305, 308.
Kraft, F., 139.
Kramers, H. A., 11, 12, 14, 373.
Kraus, I., 186.
Krauss, F., 49, 65, 176.
Krauss, G., 174.
Krebs, H. A., 289.
Kremers, H. C., 52, 53.
Křepelka, H., 43.
Kreuder, A., 160.
Kruyt, H. R., 283, 284, 294, 298, 312.
Kubel, K., 61.
Kühl, F., 178.
Kühnl, N., 285.
Kükenthal, H., 65.
Kürschner, K., 97.
Kürthy, L., 35.
Küster, W., 82, 133.
Kugelmass, 217.
Kuhn, 233, 342, 347, 355, 357.
Kuhn, A., 285, 286, 290, 293, 306.
Kuhn, R., 77, 88, 91, 108, 109, 138.
Kulenkampff, H., 256.
Kunitz, W., 263.
Kunz, E., 157.
Kunz, J., 239.
Kurckmann, E., 201.
Kurtenacker, A., 61, 179.

Laar, J. J. van, 31.
Lachman, A., 125.
Lacroix, A., 261.

Lafortune, F., 44.
Lagrave, R., 117.
Laing, (Miss) M. E., 316, 317.
Lambert, R. H., 293.
La Mer, V. K., 32.
Lamparter, W., 108.
Landauer, 338.
Lane, J. H., 187.
Lang, R., 171.
Langdon, G. M., 315.
Lange, H., 108.
Langenbeck, W., 157.
Langmuir, I., 25.
Lapworth, A., 80, 186.
Laqueur, E., 332.
Larison, E. L., 178.
Larsen, E. S., 261, 278.
Lassieur, A., 190.
Lattey, R. T., 36.
Laubengayer, A. W., 54, 55.
Lazareff, 345, 359.
Lazier, W. A., 21.
Leathes, J. B., 326.
Leavenworth, C. S., 212.
Lebeau, P., 53, 181.
Lebediantzev, A. N., 211.
Le Blanc, M., 337, 338, 339, 340, 350, 351, 361, 369.
Lecher, H., 103.
Lechner, M., 106.
Le Fevre, 230.
Legendre, R., 180.
Legg, V. H., 98.
Le Guyon, R. F., 178.
Lemmermann, O., 201, 210.
Lenher, S., 329.
Lenher, V., 61, 62, 178.
Leone, P., 170, 185.
Lessing, R., 176.
Le Sueur, 81.
Levene, P. A., 213, 237.
Lévy, J., 117.
Lévy-Lajeunesse, 218.
Lewis, G. N., 12, 13, 14, 28, 29, 30, 38.
Lewis, H. P., 188
Lewis, W. C. McC., 14, 371.
Liebl, F., 144.
Liebermann, 134.
Liempt, J. A. M. van, 62.
Liepatov, I. S., 309.
Liepe, J., 70.
Liesche, O., 107.
Liesegang, R. E., 199.
Lipschitz, 351.
Linckh, E., 57.
Lind, S. C., 47, 275.
Linder, 347.
Lindner, J., 184.
Ling, A. R., 91, 92, 93, 96.
Linhart, G. A., 29.
Linnell, W. H., 83.
Lippmann, 144.
Lochte, H. L., 184.
Locquin, R., 160.
Löwenstein, L., 180.
Löwenthal, H., 307.
Lohmann, W., 205, 225.
Lohr, A., 162.
Long, J. S., 328.
Lorah, J. R., 300.
Lorentz-Zienkovska, H., 303.
Lorenz, R., 179, 330.
Loring, F. H., 64.
Lormand, C., 185.
Lottermoser, A., 287.
Lowry, H. H., 329.
Lowry, T. M., 67.
Lucasse, W. W., 28.
Ludlam, 362.
Lueck, R. H., 16.
Lütkemeyer, 343, 367.
Luff, G., 172, 173, 175.
Lukas, J., 172, 190.
Lumière, A., 281.
Lundegårdh, H., 211, 215.
Lundsgaard, 224.
Lunn, J. W., 275.
Luther, 339, 342, 360.
Lyon, T. L., 207.

McAulay, J., 30, 35.
McBain, 315.
MacCallum, P., 304.
McCance, 235.
McCandless, J. M., 178.
McHaffie, I. R., 329.
McHugh, G. P., 110.
McKenzie, A., 116.
McKeown, A. C., 13, 16, 17, 348.
McLaughlin, H. M., 24, 322, 325.
M'Leod, 232, 233.
McMillan, A., 191.
McMullin, R. B., 69.
McQuarrie, 217.
McWillie, J., 372.
Maddison, 338.
Madsen, E., 56.
Magistad, O. C., 205.
Magnin, G., 185.
Magnuson, H. P., 206.
Mahnert, P., 25, 26.
Makamiya, 219.
Maksorov, B. V., 133.
Malik, K. S., 316.
Malinovsky, A., 271.
Manchot, W., 57, 66, 171.
Manley, J. J., 46.
Maplethorpe, C. W., 183.
Marcelin, A., 26.
Marcelin, R., 11.
Marckwald, W., 174.
Marcusson, J., 74, 206.
Mardles, E. W. J., 290.
Margosches, B. M., 179.

Margulies, C., 169.
Mark, H., 100, 245, 247, 250, 251, 252, 254, 294.
Marmasse, P., 181.
Marquis, (Mlle.) M., 56.
Marsh, J. K., 371.
Marshall, A. L., 337, 343, 356, 360, 367, 369.
Martin, T. L., 207.
Martin, W. S., 205.
Marvel, C. S., 170, 182.
Marzano, C., 309.
Mason, F. A., 140.
Matthaüs, K., 298.
Matthews, J. H., 335, 347, 350, 351, 372.
Mattil, 220.
Mattson, S. E., 200.
Maurer, K., 88.
Maxted, E. B., 19.
May, R., 48.
May, R. M., 178.
Mecklenburg, W., 329, 330.
Medsforth, S., 22.
Meerwein, H., 71, 76, 114, 129.
Mehrer, M., 144.
Mehrotra, M. R., 303.
Mehta, M. M., 97.
Meier, 225.
Meis, H., 106, 107.
Meisenheimer, J., 106, 107, 108, 109, 113, 121, 123.
Mellon, M. G., 170.
Mélon, J., 277.
Menten, M. L., 233.
Menzies, A. W. C., 44.
Merrill, G. P., 261.
Merwin, H. E., 252, 254, 268.
Merz, A. R., 178.
Messmer, E., 100.
Metz, L., 65.
Meulen, H. ter, 177, 185.
Meyer, H., 350.
Meyer, J., 64, 169.
Meyer, K. H., 70.
Meyer, R., 307.
Meyer, R. J., 177.
Meyerfeld, J., 169.
Meyhof, 225, 226.
Michael, A., 126.
Michaelis, L., 233, 281, 295, 301.
Miethe, A., 48.
Milas, N. A., 76.
Milau, E. F., 316.
Milbauer, 338, 350.
Millar, W. G., 293.
Miller, E. J., 332.
Miller, R. C., 180.
Millikan, R. A., 39.
Mills, W. H., 112, 113, 138, 143.
Minakami, R., 316.
Minganti, 347.
Miravalles, R., 329.
Mirsky, 237, 238.
Mockeridge, F. A., 211.
Modern, F., 312, 313.
Mörner, 132.
Mohs, F., 275.
Moles, E., 329.
Monforte, F., 114.
Montagne, M., 135.
Moog, L., 87.
Moor, F., 303.
Moore, C. W., 78.
Moore, H. R., 334, 359.
Morávek, V., 215, 284.
Morel, G., 68.
Morgan, C. G. T., 198.
Morgan, G. T., 73, 79, 81.
Morgan, J. W., 325.
Morgan, S. O., 329.
Morosow, N. I., 286.
Morozewicz, J., 276.
Morrell, R. S., 23, 319.
Morris, G. H., 93.
Morris, V. M., 170.
Morse, C. W., 188.
Mortimer, F. S., 38.
Moser, L., 174, 176.
Mosettig, E., 150.
Mottram, E. M., 80, 186.
Muehlberger, C. W., 62.
Müllbauer, F., 279.
Müller, A., 81, 143, 254.
Müller, C., 192.
Müller, E., 128, 192, 296.
Müller, F., 186.
Müller, H., 337, 343, 353, 356.
Mukerji, 336.
Mukherjee, D. H., 104.
Mukherjee, J., 372.
Mukherjee, J. N., 303, 331.
Mumm, O., 136.
Munroe, L. A., 330.
Munsell, 218.
Murray, H. D., 182, 318.

Naamlooze Venootschap Philips Gloeilampenfabriken, 56.
Naeser, W., 53.
Nagaoka, H., 48.
Name, R. G. van, 191.
Nanji, D. N., 91, 92, 96.
Nanji, D. R., 210.
Naryschkin, N. A., 133.
Nasaroff, 338.
Neale, S. M., 100, 318, 320.
Neeteson, P. A., 187.
Negelein, E., 356, 371.
Neidig, R. E., 206.
Nelson, 216, 218.
Nenitzescu, C., 133.
Nernst, W., 354, 357, 358, 361, 366, 372.
Neuberg, 92, 225.

Neubert, H., 309.
Neumann, F., 271.
Newbery, G., 185.
Newitt, D. M., 180.
Nicholls, F. H., 62.
Nichols, M. L., 169, 188.
Niklas, H., 193, 201, 204.
Nikolić, N., 43.
Nishina, Y., 189.
Noddack, W., 63, 335, 337, 354, 355, 357, 361.
Noll, A., 171.
Nolte, O., 199, 201.
Nonhebel, G., 28, 33.
Norberg-Schulz, C., 61.
Norris, E. R., 314.
Norris, F. W., 213.
Norrish, R. G. W., 17, 23, 319, 336, 337, 341, 347, 349, 350, 353, 355, 369, 370, 371.
Nostitz, A. von, 201.
Noüy, P. L. du, 189, 313, 322, 324.
Novelli, A., 170.
Noyes, A. A., 31, 32, 33, 224.
Noyes, W. A., jun., 334, 341, 359.
Nyssens, P., 178.

Oberbach, 338.
Oberhauser, F., 171.
Oberlin, M., 152.
Obladen, A., 371, 372.
O'Connell, M. T., 305.
Oddo, B., 133.
Oden, S., 293.
O'Dwyer, M. H., 213.
Oertal, 335.
Olbrich, W., 54.
Oldham, J. W. H., 85, 95.
Olivier, 350.
Olsen, C., 205.
Onslow, 235, 236.
Opdycke, L. H., 328.
Oppenheimer, F., 233, 292.
Ordelt, H., 172.
Orekhov, A., 116, 117.
Osterberg, 222.
Ostwald, W., 297, 306, 309, 322, 327.
Ottens, B., 107.
Overbeck, W., 296.
Oxholt-Howe, 339, 341, 355.
Ozawa, T., 102.

Paal, C., 116, 287.
Pacsu, E., 86.
Padelt, E., 62, 335.
Padoa, 337, 342, 347, 348, 371.
Page, H. J., 198.
Palazzo, 139.
Pallauf, F., 82.
Palmer, D. M., 20.
Palmer, W. G., 20.
Palmer, W. H., 138.
Paneth, F., 55.
Paolini, C., 191.
Papaconstantinou, B., 300.
Parker, H. C., 191, 193.
Parker, H. H., 75.
Parri, W., 182.
Parrish, J., 293.
Parry, J., 276.
Parsons, A. L., 275, 278.
Parsons, A. T., 181.
Partington, J. R., 60.
Paterson, H., 196.
Paton, F. J., 96.
Patrick, W. A., 316, 327, 328, 330, 331.
Paul, T., 123.
Pauli, W., 284, 285, 288, 312, 313.
Pauling, L., 31, 252, 257.
Pavlov, P. N., 201.
Payküll, 57.
Peachey, S. J., 112.
Pearce, J. N., 28.
Peard, G. T., 305, 323.
Pearson, L. K., 80.
Pease, R. N., 19.
Peck, A. B., 271.
Perkin, W. H., jun., 126, 127, 128, 141, 145, 147, 148, 151.
Perkins, 236.
Perreau, G., 300.
Perren, E. A., 129.
Perret, 336.
Perrin, J., 11, 14, 344, 354.
Petit, 53.
Petrenko-Kritschenko, P., 136.
Pfaff, 204.
Pfau, A. S., 183.
Pfuhl, W., 163.
Phillips, H., 67, 109, 111.
Phragmén, G., 252, 253.
Pick, L., 187.
Picon, M., 53.
Pictet, 95.
Pied, H., 176.
Pierre, W. H., 203.
Pike, S. R., 33.
Pinck, L. A., 186.
Pirani, M., 54.
Pirsch, H., 285, 286, 290.
Plechner, W., 169.
Plotnikov, J., 338, 339, 340, 342, 347, 351, 357.
Podjaski, G. von, 182.
Pohland, E., 251, 254.
Poirot, G., 179.
Pólányi, M., 15, 243, 247, 250, 251, 314, 327.
Poleich, G., 208.
Polonovski, Max, 154, 155.
Polonovski, Michel, 154, 155.
Ponder, E., 293.

Poole, H. J., 306.
Poore, H. D., 213.
Pope, (Sir) W. J., 112.
Popesco, J. G., 319.
Popov, M., 306.
Popov, S., 171.
Popp, K., 310.
Porlezza, C., 73.
Porter, C. R., 73.
Posner, T., 165.
Postma, J., 284.
Poulsson, 218.
Powell, A. R., 176.
Powell, S. G., 75.
Powell, W. J., 97.
Praetorius, P., 49.
Prasad, M., 299.
Prentiss, A. M., 313.
Prianischnikov, D., 212.
Prichard, C. R., 16, 22, 23.
Priess, O., 49.
Pringsheim, H., 91, 100.
Pringsheim, P., 344, 357, 361.
Pročke, O., 184.
Pryde, J., 84.
Przezdziecka-Jedrzejovska, P., 302.
Pschorr, 151.
Purdie, 84.
Purvis, C. B., 87.
Pusch, L., 355, 372.
Pyman, F. L., 145, 156, 157, 158.

Quastel, 230, 231.
Quick, W. C., 315.
Quietensky, H., 147, 151.
Quintin, M., 302.

Rabaté, H., 293.
Rabinovitsch, A. J., 302.
Rabinovitsch, E., 55.
Rackwitz, E., 299.
Radcliffe, L. G., 188.
Radel, 338.
Räth, 139.
Raikes, H. R., 67.
Ralls, 222.
Ramachandran, S., 172.
Ramage, W. D., 180.
Raman, C. V., 321.
Ramann, E., 199, 201.
Ramdas, L. A., 321.
Ramsbottom, 349.
Randall, M., 28, 29, 30, 32, 38.
Randoin, 220.
Rankin, G. A., 269.
Rankin, J., 151.
Rao, B. S., 131, 132.
Raper, 229, 235.
Raper, R., 113, 143.
Raschig, F., 57.
Rasmussen, H. B., 186.
Rauch, A., 191, 192.
Rauchalles, G., 88.
Rauchenberger, W., 89.
Ravenswaay, (Mlle.), H. J., 79.
Rây, J. N., 147.
Ray, R. C., 328.
Rebmann, A., 372.
Redlich, O., 31, 37.
Reed, 78.
Reich, 161.
Reichel, G., 174.
Reindel, F., 155.
Reinders, W., 300.
Reiser, 231.
Renner, W., 205.
Renwick, F. F., 293.
Rheinboldt, H., 122, 295, 296.
Rhodes, F. H., 188.
Ribaud, 340.
Rice, J., 11, 12, 13, 14, 16.
Richards, C. E., 172.
Richards, M. B., 178.
Richards, T. W., 38.
Richardson, A. C., 116.
Richardson, H. L., 330.
Richardson, O. W., 39.
Richmond, H. D., 179.
Richter, A., 170.
Richter, E., 70.
Rideal, E. K., 14, 16, 21, 24, 25, 26, 27, 322, 324, 326, 336, 341, 347, 352, 355, 370, 371.
Ridge, B. P., 102.
Riding, R. W., 47.
Ridley, G. N., 196.
Riede, W., 211.
Riegel, E. R., 311.
Riesenfeld, E. H., 60.
Rinne, F., 252, 270.
Roake, C. E., 179.
Rocasolano, A de G., 300.
Roberts, K. G., 69.
Robertson, G. J., 83.
Robertson, P. W., 330.
Robinson, 233, 235, 236, 347, 356.
Robinson, E., 127, 128.
Robinson, F. W., 371.
Robinson, G. M., 80.
Robinson, G. W., 204.
Robinson, P. L., 43, 45.
Robinson, R., 80, 139, 147, 183, 255.
Robison, 221.
Rodebush, W. H., 11, 32.
Rodillon, 182.
Rodt, V., 175.
Röhre, K., 173.
Röhrig, H., 251.
Roger, M., 116, 117.
Roger, R., 116.
Rogers, A. F., 278.
Rojahn, 159.

Roleff, H., 122.
Rolf, I. P., 213.
Roller, 211.
Romeo, G., 185.
Rose, 84.
Rosenberg, A., 296.
Rosenheim, M. C., 239.
Rosenheim, O., 217, 219, 238, 239.
Rosenthal, A., 308.
Rosenthaler, L., 187.
Ross, J. F., 175.
Ross, W. H., 178, 370.
Rosseland, S., 13, 364.
Rossi, G., 301.
Roth, W. A., 53.
Rousseau, E., 190.
Roy, S. C., 14.
Roylance, J., 157.
Rudberg, E., 355, 371.
Ruer, R., 44.
Ruff, O., 49, 54, 65, 176, 329.
Runge, H., 304.
Rupe, H., 160.
Russell, A. S., 51, 171.
Russell, W. W., 22.
Ruzicka, L., 118, 144.
Ryschkewitsch, E., 54.

Sabalitschka, T., 174.
Sachs, G., 251.
Saeger, A., 211.
Salabarton, 231.
Salway, A. H., 153.
Samec, M., 317.
Sammet, K., 210.
Sander, E., 199.
Šandera, K., 177, 319.
Saneyoski, 92.
Sanyal, 344.
Sas, F. E. R., 186.
Sasaki, N., 370.
Sass, L. von, 161.
Sauer, E., 307.
Saville, W. B., 254.
Saway, K., 150.
Sawjaloff, 234.
Scarth, G. W., 307.
Scatchard, G., 28, 29, 32, 33.
Schäfer, J., 129.
Schärer, O., 30, 32.
Schaffganz, 338.
Schantl, E., 169.
Schaum, K., 309, 338.
Scheffer, F., 205.
Scheiderer, S., 175.
Scheinost, E., 179.
Schenk, R., 55.
SchererP. C., 184.
Scheringa, K., 169.
Scherpenberg, A. L., van, 187.
Scheuing, A., 125.
Schiebold, E., 251, 252.
Schleicher, A., 190, 192.
Schlenk, W., 123, 124, 126.
Schlubach, H. H., 88, 89.
Schmalfuss, H., 82, 181.
Schmid, E., 251.
Schmid, L., 138.
Schmidt, E., 73.
Schmidt, G., 54.
Schmidt, J., 138.
Schmidt, R., 71.
Schmitt, 351.
Schmitz, B., 178.
Schoder, F., 82.
Schoeler, A., 152.
Schöller, V., 70.
Schöller, W., 355.
Schoeller, W. R., 176.
Schoep, A., 276, 277.
Schofield, R. K., 25, 324.
Schollenberger, C. J., 191.
Scholtz, M., 160.
Schonborn, H., 293.
Schoorl, N., 187.
Schorigen, P., 122, 126.
Schou, S. A., 186.
Schrader, 206.
Schramm, E., 293.
Schreiner, 239.
Schroter, K., 293.
Schryver, S. B., 91, 96, 104, 213.
Schuch, A., 192.
Schuckenberg, A., 205.
Schütze, M., 113.
Schulcke, C., 205.
Schulek, E., 177, 179, 185.
Schultze, K., 320.
Schulz, R. G., 322.
Schulz, W., 177.
Schulze, 217.
Schulze, F., 183.
Schulze, H., 327.
Schwab, G. M., 59.
Schwarz, R., 194.
Schweizer, 235.
Scott, 221.
Scott, W. W., 172, 179.
Scott-Blair, G. W., 311.
Scripture, jun., E. W., 293.
Sease, V. B., 293.
Seide, O., 138, 139.
Seidel, C. F., 144.
Seifert, W., 287.
Seisov, K., 306.
Seith, W., 321.
Seitz, F., 153.
Seka, R., 152.
Semper, L., 166.
Sen, K. C., 299, 302, 303, 304.
Seto, K., 278.
Sever, W., 327.
Shannon, E. V., 261, 277.
Sharp, 340.
Sharples, E. H., 188.

Shaw, B. D., 135.
Shaw, P. E., 324.
Shaw, W. S., 210.
Shaxby, J. H., 248.
Shearer, G., 81, 196, 254, 255.
Shearman, L. P., 75.
Shepherd, E. S., 269.
Sherman, 218.
Shikata, M., 40.
Shukov, I. I., 305.
Shute, W. J., 341, 371.
Sidener, C. F., 176.
Sidgwick, N. V., 70.
Siedentopf, H., 283, 294.
Sieper, 349, 351.
Silber, P., 118.
Simms, 237.
Simon, L. J., 81.
Simonnet, 220.
Simonsen, J. L., 131, 132.
Simpson, E. S., 278.
Singer, R., 101.
Sinozaki, H., 54.
Sittig, L., 58.
Sjörslev, 218.
Skraup, H., 109.
Slansky, P., 82.
Slater, 233.
Slater, A. V., 298.
Smedt, J. de, 251.
Smiles, S., 112.
Smith, 210, 224.
Smith, A. M., 201.
Smith, D. F., 12, 13, 14, 16.
Smith, F. E., 182.
Smith, G. F., 175.
Smith, H., 216.
Smith, J. L. B., 143.
Smith, R. B., 284.
Smolik, L., 204.
Smorodincev, I. A., 307.
Snyder, E. F., 188.
Sörensen, M., 313.
Sörensen, S. P. L., 312, 313.
Sokolov, A., 204.
Solaja, B., 173.
Someya, K., 171, 176.
Sottery, C. T., 169.
Soule, B. A., 174.
Souther, B. L., 135.
Spacu, G., 168, 172, 173.
Spängler, T., 188.
Späth, E., 142, 147, 150, 151, 152, 153, 157.
Speas, W. P., 373.
Spek, J. van der, 202.
Spencer, 341.
Spencer, D. A., 59.
Spencer, L. J., 275, 276.
Speyer, E., 152.
Spielmann, P. E., 262.
Spielmeyer, G., 162.
Stadnikov, G., 285.
Staechelin, E., 372.
Stafford, J., 329.
Stamm, A. J., 294.
Stammreich, H., 48.
Stanley, E., 156.
Stark, 360.
Staudinger, H., 74, 118, 120, 125.
Stauf, W., 297.
Stedman, E., 154.
Steenbock, 216, 217, 218.
Steigmann, A., 169.
Steiner, A., 322.
Steinheil, M., 43.
Stephen, H., 70.
Stephenson, 230, 231.
Stephenson, G. E., 43.
Stern, 230, 358, 363, 368.
Stevens, T. S., 145.
Stewart, 225.
Stewart, C. P., 104.
Stewart, L., 19.
Stiasny, E., 305.
Stobbe, H., 351, 372.
Stock, A., 49, 50.
Stocks, H. B., 308.
Stoermer, R., 109, 372.
Stoppel, A. E., 176, 177.
Strache, H., 208.
Strachoff, von, 335.
Strauch, G., 46.
Straus, F., 154.
Stschoukarev, S. A., 305.
Stuckardt, 339, 351.
Stuckert, G. V., 311.
Sturgis, R. D., 28.
Sudborough, J. J., 67.
Sugden, S., 23, 77, 78, 321.
Sundius, N., 268.
Suszko, J., 144.
Sutton, T. C., 181.
Švéda, J., 181, 184.
Svedberg, T., 294.
Swanson, C. O., 196.
Swensson, 351.
Swift, E. H., 175.
Syniewski, V., 89, 90.
Szent-Györgi, 227.
Szidon, V., 297.

Tacke, I., 63.
Täufel, K., 185.
Tafuri, G. B., 185.
Tague, E. L., 313.
Takahashi, 219.
Tallyn, W. H., 73.
Tamburini, 139.
Tammann, G., 257, 260.
Tananaev, N. A., 168, 173.
Tartar, H. V., 300.
Tavernier, P., 187.
Taylor, 341, 350.
Taylor, G. I., 249, 251.

Taylor, H. A., 23, 371.
Taylor, H. S., 17, 18, 19, 21, 22, 331, 338, 360, 366, 367, 369.
Taylor, M. C., 69.
Taylor, N. W., 38.
Taylor, W., 337, 340.
Tazelaar, 216.
Teichmann, L., 54.
Tendeloo, H. C., 283.
Tendick, 221.
Terentiev, A., 68.
Terry, E. M., 76.
Thal, A., 124, 126.
Theodortschick, K., 36.
Thiele, J., 128.
Thiessen, P. A., 283, 308.
Thode, C., 162.
Thomas, A. W., 306, 314.
Thomas, P., 183.
Thoms, H., 68.
Thomson, (Sir) J. J., 12.
Thorne, P. C. L., 289.
Thornton, C. W., 12.
Thornton, H. G., 210.
Thornton, W. M., jun., 170.
Thorpe, J. F., 126, 128, 130.
Thunberg, 232.
Tian, 339, 341, 347, 352.
Tideswell, F. V., 207.
Tiffeneau, M., 116, 117, 118.
Tindal, S. J., 169.
Tischbein, W., 111.
Tolman, R. C., 11, 12, 13, 14, 16, 58, 348, 355, 360, 361.
Tomiček, O., 191, 192, 284.
Tomkeiev, S. I., 257.
Tomkinson, (Miss) M. G., 138.
Tomoda, Y., 68.
Topley, B., 23.
Toussaint, C., 56.
Toussaint, L., 190, 192.
Tramm, 47, 337, 349, 368.
Tramm, H., 370.
Tranton, W., 125.
Traube, J., 25, 299.
Trautz, 335, 337, 347.
Travers, A., 63.
Treadwell, W. D., 191.
Trénel, M., 205.
Trillat, J. J., 255, 294, 317.
Tritt, C., 144.
Tröger, J., 142.
Troje, E., 187.
Trümpler, 361.
Tschelincev, V. V., 133.
Tschitschibabin, A. E., 138, 139, 142, 155.
Tschugaev, L., 170.
Tsujimoto, M., 80.
Tuchel, 338.
Tunnicliffe, H. E., 104, 225.
Turner, E. E., 113.
Tutin, 81, 213.
Tutton, A. E. H., 255, 256.

Uhland, R. E., 207.
Uhlenbruck, P., 288.
Ulich, H., 36.
Umney, J. C., 132.
Ungerer, E., 201.
Urbain, E., 329.
Urbain, G., 56.
Urbain, P., 56.
Urk, H. W. van, 182.
Usher, F. L., 59.
Uspenski, N., 250.
Utzino, S., 286.

Vági, S., 170, 206.
Valkenburgh, H. B. van, 58.
Valkó, E., 284.
Valton, P. A., 182.
Vanderhook, G., 175.
Vanselow, A. P., 32.
Vassar, H. E., 278.
Vavon, G., 19.
Vellinger, E., 306.
Venable, F. P., 45.
Venkataramaiah, 338.
Verbruggen, L., 44.
Verley, A., 72.
Vernadsky, W., 259.
Vickery, H. B., 212.
Vidic, E., 65, 176.
Vieweg, W., 99.
Vigneaud, V. du, 170.
Vilbrandt, F. C., 54.
Villa, L., 296.
Villiger, V., 121.
Vilsmeier, A., 143.
Vinney, S. S. de, 256.
Vinson, C. G., 212.
Visscher, 224.
Vita, N., 371.
Vivario, R., 184.
Vlès, F., 188, 306.
Vogel, I., 37, 60, 61.
Vogel, W., 183.
Volmar, 341.
Volmer, M., 25, 26, 323, 338, 358, 359, 361, 363, 368.
Vonderwahl, E., 143.
Vongerichten, 143.
Vortmann, G., 184.
Vranek, J., 355, 371.
Vuilleumier, E. A., 186.

Wachendorff, E., 330.
Waele, A. de, 298.
Wagner, C., 185.
Wagner, E. C., 177.
Wahlbaum, H., 132.
Waksman, S. A., 207, 208, 209.
Walcker, R., 194.

Walden, P., 36, 109.
Waldmann, H., 332.
Walker, T. L., 275, 277, 278.
Walker, W. B., 173.
Wallach, O., 118.
Walther, T., 286.
Wangler, J. G., 212.
Warburg, E., 334, 340, 352, 354, 355, 356, 358, 359, 361, 362.
Warburg, O., 371.
Wardlaw, W., 62.
Ware, A. H., 183.
Warington, (Miss), 210.
Warren, E. H., 112.
Wartenburg, H. von, 60, 65, 182.
Washington, H. S., 259, 260, 268.
Wasteneys, 234.
Watson, 218.
Watson, D. L., 16.
Weber, 60.
Weber, A. P., 256.
Weber, B., 175.
Weber, J., 76.
Webster, 216, 217.
Wechter, E. J., 62.
Weeldenburg, J. G., 174.
Wehmer, C., 206.
Wehrmann, O., 205.
Weibezahn, K., 166.
Weickel, T., 123.
Weidemann, 218.
Weidenkaff, E., 116.
Weigel, O., 196.
Weigert, F., 337, 338, 340, 341, 350, 353, 355, 356, 359, 360, 362, 363, 367, 368, 372.
Weimarn, P. P. von, 282, 283, 286, 287, 290, 308, 311.
Weinland, 233.
Weinstock, 216, 217.
Weir, A. B., 301.
Weissberg, J., 117.
Weissenberg, K., 247, 249, 250.
Weissenberger, G., 332.
Weismantel, J., 163.
Weltzien, W., 101.
Wendehorst, E., 175, 177.
Wendt, 338.
Werner, A., 106, 112.
Werner, H., 181.
Werner, O., 36.
Wesly, W., 192.
West, E. S., 182.
Westgren, A., 252, 253.
Wever, F., 248.
Wheeler, R. V., 98, 207.
Wheeting, L. C., 199.
Wherry, E. T., 266.
Whetham, 230, 231.
Whiston, 336, 337, 345.
White, E. C., 16, 58.
White, J. W., 184.
Whitman, J. L., 171.
Whittaker, H., 77, 97.
Wibaut, J. P., 138.
Wick, R. M., 18.
Widgoff, L., 311.
Widmer, R., 134.
Wiedbrauck, E., 330.
Wiegner, G., 199, 287.
Wieland, H., 103, 152, 166.
Wierda, J., 52.
Wiessmann, H., 210.
Wightman, E. P., 293.
Wigner, E., 15.
Wilbur, O. C., 185.
Wilcke, G., 189.
Wild, W., 117.
Wilde, jun., H. D., 184.
Wilke-Dorfurt, E., 295.
Wilken, D., 65.
Wilkins, 78.
Wilkinson, J. A., 201.
Williams, 341, 352, 355.
Williams, E. G., 370.
Williams, R., 204.
Williams, W., 198.
Williamson, R. V., 351, 372.
Williamson, W. T. H., 301.
Wills, G. O., 116.
Willstätter, R., 153.
Wilson, B. D., 207.
Wilson, H. C., 314.
Winchell, A. N., 265, 266, 267.
Winkler, L. W., 169, 179.
Winter, 224.
Winter, F. A., 174.
Winter, H., 177.
Winterstein, 217.
Wintgen, R., 307.
Winther, C., 334, 335, 339, 341, 343, 348, 350, 351, 355, 356, 357, 362, 372.
Withers, 81.
Wittekindt, W., 161.
Wöhler, L., 65.
Wölfel, E., 142.
Wolf, A., 86.
Wolf, H., 173.
Wolf, L., 58.
Wolff, C. J. de, 187.
Wolfsohn, 91.
Wolkenberg, A., 295.
Wood, 344.
Wood, J. G., 215.
Wood, R. W., 373.
Wood, W. A., 252.
Wooldridge, 231.
Wormall, 235.
Worrall, D. E., 165.
Wortmann, R., 114.
Wrede, 239.
Wright, 222.
Wright, F. E., 269, 276.
Wright, W. M., 21.
Wróbel, A., 189.

Wu, D. Y., 313.
Wu, H., 313.
Wulf, O. R., 16.
Wurmser, 339.
Wyckoff, R. W. G., 18, 22, 243, 252, 254.

Yajnik, N. A., 316.
Yardley, K., 78, 255, 256.
Yontz, M. A., 67.
Yumikura, S., 307.

Zacharias, L., 296.
Zacharias, P. D., 281.
Zambonini, F., 266, 277, 278.
Zamparo, A., 183, 184.
Zies, E. G., 269.
Zikes, H., 208.
Zimmermann, 224.
Zintl, E., 45, 48, 191, 192.
Zocher, H., 291, 294.
Zschiegner, H. E., 176.
Zsigmondy, R., 288.

INDEX OF SUBJECTS

Acceptors, collisions with, 363.
Acetals, formation of, 69.
Acetic acid, ethyl ester, preparation of, 69.
*di*chloro-, preparation of, 75.
Acetoacetic acid, ethyl ester, preparation of, 69.
structure of, 70.
Acetone, detection of, 182.
Acid, $C_{22}H_{36}O_2$, from algæ, 80.
Acids, fatty, formation of, from paraffins, 74.
and their esters, spreading of, on water, 26.
higher fatty, 78.
surface tension of, 326.
unsaturated fatty, 75.
Activation, 359.
Activity coefficients, 28.
Adrenaline, estimation of, 186.
Adsorption, 17, 326.
hydrolytic, 331.
from gases, 327.
from solutions, 330.
Aetioporphyrin, structure of, 133.
Afwillite, 276.
Agar-agar gels, swelling capacity of, 309.
Albumin, precipitation of, 314.
Alcohols, 67.
synthesis of, 68.
catalytic dehydrogenation of, 20.
asymmetric tertiary, preparation and dehydration of, 68.
Aldehydes, synthesis of, 70.
reduction of, 71.
hydroxy-, 71.
Aldoximes, configuration of, 107.
Alkali metals, separation of, 175.
Alkaloids, cinchona, 144.
*iso*quinoline, 145.
estimation of, 186.
Alkylglucosides, synthesis of, 86.
Aluminium, atomic weight of, 43.
alloys, estimation of magnesium in, 175.
silicates, 268.
detection of, 169.
estimation of, 173.
Aluminosilicates in soils, 194.
Amethyst, colour of, 273.
Amines, secondary, identification of, 182.
Amino-acids, dehydration of, 164.
Amino-alcohols, deamination of, 116.
Ammonia, solid, structure of, 252.
adsorption of, by glass, 328.
tert.-Amyl alcohol, detection of, 183.
Amylodextrin, structure and oxidation of, 89.
Amylodextrinic acid, 89.
Amylogen, formula for, 90.
Amylo-hemicellulose, 91.
Amylopectin, 92.
Analysis, diffusion, 295.
electrochemical, 190.
gas, 180.
inorganic, 168.
organic, 182.
physical, 188.
water, 179.
Andalusite, 268.
Andropogon Jwarancusa, Δ^4-carene from, 131.
Aniline, estimation of, 188.
Anilines, detection of, 182.
ω-Anilinoacetophenone, hydrazones of, 111.
3-Anilino-5-keto*iso*oxazole, 165.
4-Anilino-1-methyl-2-methylene-1 : 2-dihydroquinoline, 142.
Anodes, 190.
Anthracene, estimation of, 188.
Antimony, estimation of, 190.
Aporphine, synthesis of, 152.
Arabinose, and its derivatives, structure of, 83, 85.
Arachidic acid, synthesis and structure of, 81.
Arsenic, colloidal, 286.
*tri*sulphide sols in organic liquids, 289.
organic compounds, optically active, 113.
estimation of, 185.
separation of, from antimony, 173.
Ascaris lumbricoides, metabolism of, 233.
Atomic weights, 42.
Autoxidation, 117.

Bacillus coli, action of, 230.
Bacillus pyocyaneus, fermentation by, 231.
Bacteria, chemistry of, 230.
Barbituric acid derivatives, detection of, 183.
Bardolite, 276.
Barium chloride, activities of, 28.
*tri*oxide, 50.
Barytes, structure of, 252.
Bases, organic, detection of, 183.
Beckmann rearrangement, 106.
Beer, surface tension of, 323.
Behenic acid, sodium salt, unstable states of, 316.
Benjaminite, 277.
Benzaldehyde, action of sodium on, 125.
estimation of chlorine in, 187.
Benzoic acid, esters, action of sodium on, 124.
Berberine, structure of, 147.
Beryllium, preparation of, 49.
sulphate, hydrates, 49.
Biosterin, 219.
Biotite, 263.
6 : 7 : 3′ : 4′-Bismethylenedioxy-3 : 4-dihydroprotopapaverine, 146.
Bismuth, atomic weight of, 46.
colloidal, 285, 290.
estimation of, 192.
estimation and separation of, 172.
Blood, sugar in, 224.
Boron, atomic weight of, 43.
preparation of, and a new oxide, 51.
new chloride of, 50.
Boric acid, estimation of, 177.
Borates, 51.
Brass, corrosion of, in sea-water, 48.
Bromellite, 277.
Bromine, atomic weight of, 44.
in volumetric analysis, 171.
Bromides, estimation of, 192.
Bromo-acids, action of alkalis on, 128.
Bromoazoimide, 59.
*cyclo*Butane derivatives, 126.
*dl-iso*Butyric acid, *αβ-di*hydroxy-, 75.

Cacao fat, glycerides of, 79.
Cadaverine, 239.
Cadmium, separation of, from zinc, 172.
Calcites, coloured, 273.
Calcium carbonate hexahydrate, 50.
chloride, activity of, 28.
hydride as reagent for ketones, 73.
estimation and separation of, 174.
Cannizzarite, 277.
3-Carbethoxy-2 : 4-dimethylpyrrole-5-vinyl-ω-carboxylic acid, 133.
Carbocyanines, reduction of, 144.
Carbon, atomic weight of, 42, 43.
melting point of, 53.
amorphous, nature of, 54.
*mono*xide, catalytic oxidation of, 22.
*di*oxide, heat of formation of, 20.
solid, structure of, 251.
reduction of, by hydrogen, 23.
estimation of, 181.
estimation of, in water, 179.
estimation of, in organic compounds, 184.
Carbonado, heat of combustion of, 53.
p-Carboxyphenylmethylethylarsine sulphide, 113.
Carene, occurrence of, 131.
Capillarity, 318.
Casein, 314.
Catalysis of gas reactions, 22.
promoter action in, 21.
heterogeneous, 17.
Catalysts, Röntgen-ray structure of, 18.
poisoning of, 19.
Catalytic hydrogenation, 20.
Cathodes, dropping mercury, electrolysis at, 40.
Cells, electrochemical, 39.
Cellite, 102.
Cellobiose, 101.
Cello*iso*biose, 102.
Cellodextrin acetates, 101.
Cellulose, 98.
crystal structure of, 243.
dispersion of, 287.
acetolysis of, 101.
oxidation of, 102.
*tri*acetate, 102.
Cellulose A, methylation of, 101.
Cerium, preparation of, 52.
Cetyl alcohol, preparation of, 67.
Chapmanite, 277.
Charcoal, adsorption by, 329, 331.
adsorption and catalysis by, 21.
Chemical reactions, mechanism of, 11.
Chemiluminescence, 364.
Chitin, crystal structure of, 245.
Chloramine T in analysis, 170.
Chlorine, atomic weight of, 44.
photochemistry of, 336, 368.
as negative photosensitiser, 350.
higher oxide of, 62.
Hydrochloric acid, activity of, 28.
Chlorides, estimation of, 192.
Chlorates, estimation of, 177.
Chlorous acid, estimation of, 192.
Hypochlorous acid, estimation of, 192.
estimation of, in benzaldehyde, 187.
estimation of, in water, 179.
Chlorophæite, colours of, 274.

Chlorophœnicite, 277.
Cholesterol, effect of ultra-violet rays on, 217.
synthesis of, in the animal organism, 218.
effect of, on surface tension of water, 326.
Cinchona alkaloids, 144.
Citric acid, detection of, 182.
Citrine, colour of, 272.
Claisen condensation, 73.
Clays, 199.
dispersion of, 287.
Cobalt amide and nitride, 64.
hydroxide, colloidal, 287.
detection of, 169.
estimation of, 174.
estimation of, in nickel salts, 189.
Cobaltammines, complex, activity coefficients of, 32.
Cod liver oil, assay of vitamins in, 218.
Colloids, classification of, 281.
refraction of, 292.
coagulation of, 300.
dialysis of, 295.
freezing of, 292.
peptisation of, 298.
swelling and dispersion of, 290.
ultrafiltration of, 296.
lyophilic, hydrogen-ion concentration of, 283.
protective, 286, 299.
Colloidal particles, electric charge on, 294.
solutions, viscosity of, 297.
sensitisation of, 303.
suspensions, size of particles in, 293.
systems, properties of, 291.
anisotropy of, 294.
Colouring matters, electrocapillary analysis of sols of, 320.
Columbium, separation of, 175.
Condensers, dark-field, 294.
Copper, atomic weight of, 44.
corrosion of, in sea water, 48.
catalytic, poisoning of, by mercury, 19.
promoter action of palladium on, 21.
alloys with zinc, structure of, 253.
detection of, 168.
detection of, in water, 179.
estimation of, 191.
Copper, separation of, 172, 190.
n- and *iso*-Corybulbines, 149.
Corycavamine, 148.
Corycavidine, 148.
Corycavine, 148.
Corydaline, 148.
Corypalmine, 150.
Cosmochemistry, 261.
Cotton, analysis of, 187.
Cotton wax, alcohols from, 68.
Coumarin, estimation of, 188.
Crystals, classification of, 240.
refractive index of, 257.
Röntgen-ray reflexion by, 258.
aggregate, structure of, 246.
single metallic, effect of stress on, 249.
Cuskhygrine, 134.
Cutch, analysis of, 186.
Cutic acid, 98.
Cutin, 98.
Cutinic acid, 98.
Cyanamide, estimation of, 186.
*iso*Cyanilic acid, 103.
Cyanogen :—
Hydrocyanic acid, vapour pressure of, 54.
potassium and sodium salts, purification of, 48.
Cytochrome, 238.

Desmotropy, ketocyclic, 71.
keto-enolic, 70.
Dextrins, 90.
synthetic, 95.
Dextrose, structure of, 83, 85.
Diacetyl-ψ-glucal, 87.
Dialysis, 295.
Diamond, heat of combustion of, 53.
Diborane, structure of, 254.
d-Dicentrine, 151.
Dielectric constants and concentration, 33
of electrolytes, 36.
Diffusion analysis, 295.
Diglucosan, structure of, 95.
1 : 8-Dihydronaphthyridine, 139.
1 : 2-Dihydroquinaldine, 140.
Di-indazole, *di*-3-hydroxy-, 162.
δ-Diketones, enolisation of, 135.
3 : 5-Diketopyrazolidines, 158.
1 : 8-Dimethyldibenzocopyrine, 10 : 15-*di*amino-, 139.
1 : 5-Dimethylglyoxaline, synthesis of, 158.
Dimethylketen, polymerisation of, 74.
Diopside, structure of, 252.
Diphenylethylene moloxide, 120.
Diphenylketen *mon*oxide, 120.
Di*iso*propylidenemannosylamine, 86.
Disaccharides, 88.
Driers, mechanism of action of, 82.
Dvi-manganese, 63.

Earth, composition of the crust of, 259.
chemistry of the interior of, 260.
Earths, rare, separation of, 52.

Eka-manganese, 63.
Elæostearic acids, structure of, 79.
Elatolite, 278.
Electrical conductivity of strong electrolytes, 36.
Electrodes, antimony, 191.
mercurous chloride (*calomel*), 190.
Electro-dialysis, 295.
Electrolysis with dropping mercury cathodes, 40.
Electrolytes, dielectric constants of, 36.
strong, 27.
conductivity of, 36.
Elements, Nos. 43 and 75, 63.
Ellsworthite, 278.
Emulsions, size of globules in, 294.
Enols, determination of, 70.
Enzyme action, 233.
Equation of state for the Gibbs layer, 25.
Equilibria, membrane, 41, 314.
Erbium nitride, 58.
Etched figures, 257.
Ethane, structure of, 254.
Ethoxide, aluminium, syntheses with, 72.
Ethyl alcohol, dehydration of, 67.
hypochlorite, preparation of, and its reactions with organic compounds, 69.
Ethylene, autoxidation of, 118.
chlorohydrin, action of sodium cyanamide with, 163.
Evaporation and capillarity, 320.

Fats, spreading of, on water, 324.
oxidation of, 225, 229.
Ferrous salts. *See under* Iron.
Fibrolite, 268.
Films, structure of, 323.
on surfaces, 26.
unimolecular, 325.
Flocculation meter, 293.
Fluorine :—
Hydrofluoric acid, activity of, 28.
estimation of, 177.
Formaldehyde, alkaline condensations with, 82.
detection of, 182.
estimation of, 185.
Formic acid, calcium salt, structure of, 255.
Foshagite, 277.
Fourmarierite, 277.
Fumaric acid, structure of, 255.
conversion of maleic acid into, 76.
action of bacteria on, 231.
Furoxan, *di*cyano-, 103.

Galactose, structure of, 85.
Galactosidoglucose, 89.
Gallium hydroxide and sulphate, 51.
separation of, 175.
Gambier, analysis of, 186.
Gases, adsorption of, 327.
catalysis of reactions of, 22.
Gas analysis, 180.
Gelatin, 304.
surface tension of, 325.
protective action of, 300.
purification of, 296.
swelling of, in acids, 314.
gels, elasticity of, 306.
swelling and shrinkage of, 308.
Geochemistry, 259.
Germane, 54.
Germanium, estimation of, 175.
Germanium glass, 55.
Glass, adsorption by, 328.
germanium, 55.
Gliadin, isoelectric point of, 313.
β-Glucosan, structure of, 85.
polymerisation of, 95.
Glucosans, 95.
Glucose. *See* Dextrose.
Glucosides, 87.
β-Glucosidomaltose, 92.
Glue, purification of, 297.
Glutaric acid, αα′-*di*bromo-esters, condensation of, 127.
Glutathione, 225.
synthesis of, 104.
in blood, 224.
Glutenin, isoelectric point of, 313.
Glycerol from sugar fermentation, 68.
glucoside, structure of, 87.
detection of, 182.
α-Glycols, dehydration of, 115.
Glycyrrhizin, detection of, 183.
Glyoxalines, 155.
Gold, formation of, from mercury, and its detection, 48.
colloidal, 287.
protection of, 300.
alloys with zinc, structure of, 253.
detection of, 168, 189.
estimation of, 192.
Gorngarrite, 278.
Gossypyl alcohol, 69.
Granite, weathering of, 196.
Graphite, structure of, 248.
α- and β-Graphite, heat of combustion of, 53.
Grignard reaction, mechanism of, 121.
Grignard reagents, detection of, 183.
Groups, migration of, 115.

Hæm, 237.
Hæmochromogens, 238.
Hæmoglobin, 237.
Hæmoglobins, osmotic pressure of, 314.

Hafnium, atomic weight of, 45.
properties of, and its separation from zirconium, 56.
estimation of, 189.
separation of, 176.
Halogens as photosensitisers, 348.
estimation of, in organic compounds, 184.
Heat of adsorption, 19.
Helium in discharge tubes, 47.
$\alpha\beta$-Hexa-amylose, structure of, 92.
Hexachlororuthenates. *See under* Ruthenium.
Hexosephosphates, synthesis of, 223.
Hofmann's reaction, modified, 136.
Holmium, atomic weight of, 45.
Humic acid, 206.
Hydrazine, estimation of, 192.
Hydrazones, isomerism of, 111.
Hydrides, volatile, 55.
Hydriodic acid. *See under* Iodine.
Hydrochloric acid. *See under* Chlorine.
Hydrocyanic acid. *See under* Cyanogen.
Hydrofluoric acid. *See under* Fluorine.
Hydrogen, atomic weight of, 42.
heat of adsorption of, on nickel, 19.
combination of chlorine and, 368.
combination of dried oxygen and, 47.
sulphide, laboratory preparation of, 60.
compounds of metallic halides with, 60.
estimation of, in organic compounds, 184.
Hydrogen-ion concentration, measurements of, 193.
Hydroxides, electrometric precipitation of, 172.
Hypercalcæmia, 221.

Indazoles, 161.
Indicators, 170.
dissociation constants of, 188.
for alkaloids, 186.
for water analysis, 180.
Indium, estimation of, 190.
Indole derivatives, 152.
Indoxazen, structure of, 165.
Inorganic analysis, 168.
Insulin, 223.
Interfaces, 27, 323.
Internal pressure of mixed liquids, 37.
Inulin, 212.
Invert-sugar, estimation of, 187.
Iodine, solubilities of, 38.
Hydriodic acid, adsorption of, by glass, 329.
decomposition of, 23.
Iodometry, 171.
Ionic strength, 30.
Iridium halides and *tetr*oxide, 65.
Iron :—
Ferric hydroxide sols, 285.
Ferrous nitride, 64.
selenate, compound of nitric oxide with, 57.
Steel, estimation of chromium and vanadium in, 192.
detection of, 169.
estimation and separation of, 173.
Isinglass, hydrolysis of, 104.
Isomerism, mechanism of, 113.

Jatrorrhizine, 150.
Jellies, 308.

Kempite, 278.
Keten, preparation of, 73.
autoxidation of, 118.
Ketones, reduction of, 71.
α-hydroxy-, synthesis of, 73.
4-Ketopalmitic acid, synthesis of, 80.
4-Keto-6-phenyl-1 : 2-divinylenedihydropyrimidine, 139.
10-Ketostearic acid, synthesis of, 80.
β-Keto-$\alpha\alpha\gamma\gamma$-tetramethylglutaric anhydride, 74.
Ketyls, metallic, 123.
Kino-ultramicroscope, 294.
Kochite, 278.
Kyanite, 268.

Lactacidogen, 225.
Lactarinic acid, synthesis of, 80.
Lactic acid, detection of, 182.
estimation of, 185.
Lactoles, 71.
Lactolides, 71.
Lamps, sodium, 48.
Laterites, 196.
Laudanidine, 152.
Lead, atomic weight of, 45.
estimation of, in water, 179.
estimation and separation of, 172.
Lepidolite, 263, 264.
Lichenin, 100.
Lichosan, 100.
Liesegang rings, 309.
Lignin, constitution of, 96.
Lignol, 97.
Lignosulphonic acid, 98.
Linoxyn, 82.
Linseed oil, autoxidation of, 82.
Liquids, surface properties of, 23.
surface tension of, 321.
foaming capacity of, 322.
binary mixed, activity of, 37.

Lithium, atomic weight of, 42.
chloride, activity of, 28, 34.
potassium sulphate, structure of, 253.
Lithium minerals, analysis of, 175.

Magnesium, preparation of, 49.
estimation and separation of, 175.
Magnesylpyrrole, syntheses with, 133.
Magnetites, estimation of iron in, 192.
Maleic acid, structure of, 255.
conversion of, into fumaric acid, 76.
Malic acids, chloro-, 77.
Malonic acid, ethyl ester, syntheses with, 126.
Maltodextrins, 93.
Manganese, structure of, 252.
allotropy of, 63.
oxide sols, 287.
Manganic salts, 63.
estimation of, 174.
Manganolangbeinite, 278.
Manganophyllite, 263.
Masurium, 63.
Membranes, equilibria at, 41, 314.
Mercury, capillarity of, 319.
purification of, 50.
conversion of, into gold, 48.
helide, 46.
estimation of metals in, 171.
Merrillite, 261.
Metabolism, carbohydrate, 223.
Metals, crystal structure of, 249.
rolled foils of, 250.
Metals of Group III, separation of, 174.
Metallic sulphide sols, 286.
Meteorites, 261.
Methæmoglobin, 238.
Methyl alcohol, purification and testing of, 67.
Methylamine, detection of, 182.
Methylene-blue as indicator in biology, 231.
Methylenedihydropyridines, 136.
Methylfurfuraldehyde, hydroxy-, estimation of, 187.
Methylindazoles, alkylation of, 162.
Methyl *n*-nonadecyl ketone, 81.
Methyl *n*-octadecyl ketone, 81.
Micas, 263.
Minerals, colour in, 271, 275.
radioactive, 275.
Molecules, activated, 361.
Moloxides, 118.
Molybdenum *pent*oxide, 62.
estimation of, 176.
Monosaccharides, 82.
Montanyl alcohol, 69.
Mother of pearl, structure of, 248.
Mullite, 269, 278.
Muscle, carbohydrates in, 224.
glycogen in, 225.
lactic acid in, 225.
Muscovite, 263, 265.

Naphthalene, solubilities of, 38.
α-Naphthol, detection of, in β-naphthol, 183.
α-Naphthylhydrobenzoin, dehydration of, 116.
Neodymium, preparation of, 52.
Neoglucose, 224.
Neon in discharge tubes, 47.
Nessler's solution, 179.
Nickel films, structure of, 256.
sols in organic liquids, 289.
promoter action with, 21, 22.
catalytic, structure of, 18.
hydrogenation with, 20.
estimation of, 174, 190.
Nicotine, oxidation of, 134.
Niobium nitride, 58.
Niquine, 145.
Nitrogen, atomic weight of, 43.
*di*oxide (*nitric oxide*), compound of ferrous selenate and, 57.
Nitroso-nitrogen *tri*oxide, 57.
*pent*oxide, thermal decomposition of, 15, 58.
Nitric acid, constitution of, 58.
Nitrates, detection of, 170.
estimation of, 179.
Nitrites, detection of, 170.
*tetra*selenide and *per-* and *tetra*-sulphides, 58.
estimation of, in organic compounds, 184.
Nitronium *per*chlorates, 58.
Non-electrolytes, salting out of, 35.
Nonoic acid, sodium salt, surface tension of, 322.
Novocaine, estimation of, 186.
Nucleic acids, 236.

Oils, drying of, 82.
lubricating, heats of wetting of, 320.
Oleic acid, synthesis of, 80.
estimation of, 186.
estimation of higher fatty acids in, 80.
Opium alkaloids, detection of, 183.
Organic analysis, 182.
compounds, long-chain, structure of, 254.
Organosols, 289.
Osmium *tet*roxide, 65.
detection of, 170.
Ovary, hormone from, 222.
Oxalacetic acid, esters, thermal decomposition of derivatives of, 16.

Oxazoles, 163.
*iso*Oxazoles, 165.
*iso*Oxazoline oxides, 165.
Oxidation, biological, 225, 229.
Oxidoethylene-$\alpha\beta$-dicarboxylic acids, isomeric, 77.
Oximes, isomerism of, 105.
Oxyberberine, synthesis of, 146.
Oxycelluloses, 102.
Oxycyanogen, 63.
Oxygen, influence of, on photochemical reactions, 349.
heat of adsorption of, on charcoal, 20.
combination of dried hydrogen and, 47.
detection of, 181.
estimation of, 185.
Oxylysine, 104.
Ozone, physical constants of, 59.
thermal decomposition of, 17.
catalysis of decomposition of, 349.
estimation of, 181.
Ozonides, 120.

Palladium, estimation and separation of, 176.
Palmatine, 151.
Parachor, 77.
Parathyroids, properties of extracts of, 220.
Pearls, structure of, 248.
Pectic acid, structure of, 96.
Pectins, 95, 213.
Pectinogen, 96.
Pentachlororuthenites. *See under* Ruthenium.
Pentaerythritol *tetra*nitrate, structure of, 256.
Pentosans, estimation of, 187.
Pentoses, detection of, 183.
Peptisation, 298.
Phenol, surface tension of solutions of, 24, 322.
N-Phenylbenziminophenyl ether, 114.
Phenyl *p*-diphenylyl ketone, sodium derivative, 124.
Phenylhydrazones, distinction between pyrazolines and, 160.
2-Phenylindazole-1-oxide, 3-cyano-, 162.
Phenyl-α-naphthylbenzylmethylarsonium iodide, 113.
Phenylpropiolic alcohol, preparation of, 68.
Phosphorus, and its hydride and oxide, luminescence of, 59.
Phosphoric acid, removal of, 169.
estimation of, 177.
Photocatalysts, 348, 349.
Photochemical concentration and velocity of reaction, 344.
equivalent law, 355.
induction, 352.
intensity and velocity of reaction, 342.
reactions, effect of solvents on, 350.
mechanism of, 357.
after-effects in, 353.
temperature of, 346.
inorganic, 334.
reaction chains, 365.
stationary states, 351.
Photochemistry, energetics of, 354
Photosensitisers, 348.
Photosensitivity, 339.
Physostigmine, constitution of, 153.
Phytosterol, effect of ultra-violet rays on, 217.
Pilocarpidines, 157.
Pilocarpines, 157.
Pinus longifolia, Δ^3-carene from, 131.
Pinus sylvestris, Δ^3-carene from, 132.
Piperonal, estimation of, 188.
1-Piperonylnorhydrastine, 145.
Plants, constituents of, 212.
absorption of ions by, 213.
stimulants of growth of, 211.
effect of soil reaction on growth of, 205.
effect of boron on growth of, 210.
nitrogen compounds in, 212.
phosphatides of, 213.
effect of silica on growth of, 210.
Plant cuticles, 98.
Plastein, 234.
Platinum, separation of ruthenium and, 176.
Poisoning of catalysts, 19.
Polarity of surfaces, 23.
Polarograph, 40.
Polyamyloses, 90.
Polysaccharides, 89.
Potassium chloride, activity of, 28, 34.
hydroxide, activities of, 28.
sulphite and pyrosulphite, 61.
detection of, 169.
estimation of, 189.
Potential, differences of, 39.
Praseodymium, preparation of, 52.
Precipitates, electrolytic, structure of, 248.
Precipitation, laws of, 282.
Promoters, 21.
*cyclo*Propane derivatives, 126.
Propionic acid, β-chloro-, preparation of, 75.
Proteins, 312.
molecular weights of, 313.
coagulation of, by heat, 313.
oxidation of, by glutathione, 225.
Protoberberine, 145.

Protolithionite, 265.
Protopapaverine, 145.
Protopectin, 96, 213.
Pyrazoles, 158.
Pyrazolines, reactions of potassium cyanate with, 160.
Pyridine, reduction of, 135.
derivatives, 135.
Pyridofluorene, and its derivatives, 138.
2-Pyridoneimine-1-acetic acid, 155.
Pyridylpyrroles, 137.
Pyriminazole, 139.
Pyrroles, synthesis of, 133.
Pyroxenes, 263, 267.

Quantum efficiency in photochemistry, 356.
theory in photochemistry, 354.
Quartz, structure of, 241.
colours of, 272.
Quinaldine 4-chloro-methiodide, colouring matter from, 142.
Quinaldine synthesis, 139.
*β-iso*Quinine, 144.
Quinoline derivatives, 139.
*iso*Quinoline alkaloids, 145.

Radiation theory of reactions, 14.
Radioactive minerals, 275.
Radium rays, effect of, on colour of minerals, 275.
Ramsayite, 278.
Rays, Röntgen, secondary spectra of, 256.
reflexion of, by crystals, 258.
in colloidal research, 294.
use of, in analysis, 189.
ultra-violet, growth-promoting properties of, 215.
Refractive index, influence of atomic arrangement on, 257.
Rhenium, 63.
Rickets, effect of ultra-violet rays on, 216.
Ruthenium ammine, 65.
*penta*fluoride, 65.
tetroxide, 64.
oxides, 65.
Hexachlororuthenates, 65.
Pentachlororuthenites, 65.
Tetrachlorodioxyruthenic acid, 65.
separation of platinum from, 176.
Rye, nitrogen compounds in, 212.

Saccharinic acids, 75.
Salting-out effect, 35.
Scandium nitride, 58.
Schallerite, 278.
Sea-hedgehog, spines of, 247.
Sea-water. *See under* Water.
Secretions, internal, chemistry of, 202.
Sedimentation analysis, 293.
Selenium, atomic weight of, 44.
bromides, oxybromide, and oxychloride, 61.
Selenic acid, preparation of, 62.
separation of tellurium from, 178.
Selenocyanogen, 63.
Silicon, atomic weight of, 43.
*di*oxide, devitrification of, 54.
gels, adsorption by, 328, 330.
Silicic acid sols, 284.
detection of, in water, 179.
Silicates, constitution of, 262.
Silk, artificial, crystal structure of, 245.
Sillimanite, 271.
Silver sols, 283.
alloys with zinc, structure of, 253.
iodide, colloidal, 287.
adsorption of silver salts by, 331.
Soaps, 315.
protective action of, 300.
Soap solutions, constitution and properties of, 316.
Sodalite, colour of, 275.
Sodium in electric lamps, 47.
chloride, activity of, 28, 34.
surface tension of, 325.
hydroxide, activities of, 28.
sulphite and pyrosulphite, 61.
cyanamide, action of ethylene chlorohydrin with, 163.
detection of, 169.
Soils, classification of, 196.
acidity of, 201.
effect of drying on fertility of, 211.
effect of, on plant growth, 210.
flocculation and base exchange in, 198.
boron in, 210.
carbon and nitrogen in, 207.
inorganic colloids in, 194.
humic acid in, 206.
lime requirements of, 204.
silica in, 210.
weathering of, 194.
Solubility curves, 38.
Solutions, adsorption of, 330.
concentrated aqueous, 35.
physico-chemical analysis of, 189.
Spectra, absorption, and photosensitivity, 338.
Röntgen ray secondary, 256.
Spermine, 238.
Sphene, colours of, 274.
Sponges, calcareous needles of, 247.
Starch, constitution of, 90.
constituents of, 91.
films, elasticity of, 318.
sols, 317.
hydrolysis of, 92.
compound of iodine and, 318.
Stearic acid, sodium salt, equilibrium of water and, 316.

Stearolic acid, synthesis of, 80.
Steel. *See under* Iron.
Strontium chloride, activity of, 28.
Succinic acid, action of bacteria on, 231.
Succinimide, iodo-, structure of, 255.
Sucrose, constitution of, 88.
Sugars, bacterial fermentation of, 230.
reducing, estimation of, 187.
N-Sugars, 88.
Sulphur, solubilities of, 38.
colloidal, 286.
*sesqui*oxide, 60.
Sulphuric acid, activity of, 28.
Sulphites, estimation of, 178.
Thiosulphates, standardisation of, 171.
Thionic acids, constitution of, 61.
organic compounds, optically active, 111.
estimation of, 178.
Sulphuryl chloride, thermal decomposition of, 16.
Surfaces, formation of films on, 26.
Surface tension, 320.
and concentration, 324.
Swedenborgite, 279.
Sylvestrene, occurrence of, 131.

Tannins, detection of, 183.
Tantalum, separation of, 175.
Tartaric acid, estimation of, 185.
Tautomerism, mechanism of, 113.
Tektites, 262.
Tellurium, separation of selenium from, 187.
Tetrachlorodioxyruthenic acid. *See under* Ruthenium.
Tetrahydrobenz*iso*oxazoles, isomeric, 166.
1 : 1 : 3 : 3-Tetramethyl*cyclo*butan-2 : 4-dione, 74.
Tetramminethiocyanic acid, ferrous salt, 64.
Thallium, α- and β-forms of, 52.
alloys with mercury, activity coefficients of, 38.
cobalt and nickel sulphates, structure of, 256.
Thermophotochemical reactions, 356.
Thiocarbamides, 103.
Thiohydrates, 60.
Thionic acids. *See under* Sulphur.
Thionium salts, optically active, 112.
Thiuronium salts, 103.
Thomsonite, 266.
Thyroid, active principle of, 221.
Thyroxin, 221.
Tin hydride, 55.
separation of tungsten from, 190.
Titanium :—
Titanous chloride, use of, in analysis, 191.
p-Toluenesulphinic acid, esters, optically active, 111.
Trehalose, synthesis of, 88.
Triacetylglucal, 87.
Trimethyl γ-arabinose, structure of, 84.
Trimethyl glucose, structure of, 85.
3 : 4 : 5-Triphenyl*iso*oxazoline oxide, 160.
Tripyrrylmethanes, 133.
Tritopine, 152.
Tryptophan, estimation of, 186.
Tungsten, preparation of, 62.
helide, 46.
separation of tin from, 190.
Tyrosinase, action of, 234.
Tyrosine, oxidation of, 234.

Ultrafiltration, 296.
Ultramicrons, 283.
Uranium, estimation of, 176.
Uranyl barium and silver carbonates, 62.

n-Valeric acid, preparation of, 75.
Vanadium, estimation of, 176.
Vanillin, estimation of, 188.
Varnish films, "blooming" of, 319.
Vitamin-*A*, 219.
Vitamin-*D*, 218.
Vitamin-*E*, 220.
Vitamins, 215.
Velocity of reaction, 11.
Viscosimeter, 298.
Viscosity of colloidal solutions, 297.

Walden inversion, 105.
Water, effect of, in photochemistry, 348, 368.
activity of, 28.
evaporation of, through a fatty acid film, 27.
analysis, 179.
Sea-water, salinity of, 180.
Wenzelite, 279.
Whale oil, 79.
Wood oil, Chinese, 79.

Xenon hydrate, 47.
Xylose, structure of, 85.

Yarn, wetting of, 320.

Zinc, corrosion of, in sea-water, 48.
arc, reduction with, 49.
alloys, structure of, 253.
oxide as a photosensitiser, 348.
estimation of, 174.
Zirconium, atomic weight of, 45.
properties of, and its separation from hafnium, 56.
nitride, 58.
estimation of, 189.
separation of, 176.

T
C57
.22
1925

UNIV OF MAINE
3 7550 00874935 1